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VAPOUR PHASE RADIOLYSES OF ORGANIC COMPOUNDS

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

IN PARTIAL FUIFILMENT OF THE REQUIREMENTS FOR THE DEGREE

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by

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ABSTRACT

The vapour phase radiolyses of cyclohexane, methyl cyclohexane and ethanol by Po^{210} alpha particles were investigated. The radiolyses of these compounds with the inhibitors benzene, cyclohexene and propylene were also studied.

The major single product, in all cases, was hydrogen. The yield of hydrogen was independent of dose and had G values of 8.0, 5.8 and 9.0 for cyclohexane, methyl cyclohexane and ethanol respectively.

There was a poor material balance and a steady decrease in source intensity in hydrocarbon vapour radiolyses. These were attributed to the formation of polymer which could not be measured with the present analytical system. The formation of polymer is tentatively ascribed to ion molecule reactions, since the ions formed during radiolysis have a life time of the order of 10^{-3} secs. A good mass balance and the lack of decrease in source intensity in ethanol irradiations indicate little or no polymer formation during its radiolysis.

The value of the ratio of the initial yields of cyclohexene and dicyclohexyl (= 1.67) is similar to that found in liquid cyclohexane radiolysis. This value gives an indication of the ratio of disproportionation to combination of cyclohexyl radicals.

The yields of the products resulting from the fission of the rings of cyclohexane, benzene and cyclohexene

were at least an order of magnitude greater in the vapour than in the liquid phase.

The experimental results obtained in the inhibition studies of the various systems were tested against several mechanisms and two mechanisms were found to give straight line plots. One mechanism involved scavenging of hydrogen atoms and the other involved energy transfer from the solvent to the protector. The values of the ratios of rate constants obtained for the scavenging mechanism in the various systems have similar values. The values of the rate constant ratios obtained with cyclohexene might not be unreasonable if the hydrogen atoms are epithermal. The value of the ratio of hydrogen abstraction from benzene to that from the solvent is surprisingly high even for epithermal hydrogen atoms. The various ratios of rate constants for the energy transfer mechanism also appear to have similar values except in the ethanol-benzene system. In the cyclohexane inhibition studies, the value of the ratio of the rate constants for energy transfer to that for the decomposition of the activated cyclohexane species was greater in the gas phase by a factor of about 10^3 over the value of the ratio in the liquid phase. This may be taken as evidence that the activated species is a positive ion that decomposes when neutralised.

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TABLE OF CONTENTS

	Page
I INTRODUCTION	
General	1
(A) Historical	1
(B) Concepts of Mechanisms in Radiation Chemistry	7
(a) Absorption and migration of energy	7
(1) Transfer of excitation energy	9
(2) Ionisation transfer	11
(3) Electron capture	12
(b) General mechanisms of radiolysis	13
(1) Cluster mechanism	14
(2) Burton's mechanism	14
(3) Free radical mechanism	16
(4) Ion-molecule reactions	16
(c) Inhibition mechanisms	17
(1) Scavenger studies	18
(2) Protection studies	20
(C) Survey of Previous Studies of the Radiolysis of the Compounds used in the Present Work	22
(a) Cyclohexane	22
(b) Cyclohexene	28
(c) Benzene	30
(d) Propylene	32

Page

(e) Methyl cyclohexane 32

(f) Ethanol 33

(D) Dosimetry 37

(E) Scope of the Present Work 43

II EXPERIMENTAL

(A) Apparatus 45

(a) Main Manifold 45

(b) Auxiliary manifold 49

(c) Gas Calibration manifold 50

(B) Materials 50

(a) Cyclohexane 51

(b) Benzene 51

(c) Cyclohexene 51

(d) Propylene 51

(e) Methyl cyclohexane 51

(f) Ethanol 52

(g) The alpha source 52

(C) Techniques 52

(a) Standardisation of the Po^{210} source 52

(b) Preparing the samples for irradiation 53

(c) Analytical techniques 55

(d) Calibration factors 58

(1) Hydrogen, Methane and Carbon monoxide 58

Page

(2) Gases volatile at -112°C 58

(3) Liquids 59

III RESULTS

(A) Calibrations 60

(a) The -196°C fraction 60

(b) The -112°C fraction 63

(c) Liquid products 63

(B) Irradiations 68

(a) Calibration curves 68

(b) Blank runs 71

(c) Cyclohexane radiolysis 72

(1) Radiolysis of cyclohexane as a function of volume 72

(2) Radiolysis of cyclohexane as a function of dose 75

(3) Inhibition studies 80

(d) Benzene, cyclohexene and propylene radiolyses 87

(e) Methyl cyclohexane radiolysis 90

(1) Radiolysis of methyl cyclohexane as a function of dose 90

(2) Inhibition studies of the methyl cyclohexane systems 93

(f) Ethanol radiolysis 97

(1) Radiolysis of ethanol as a function of dose 97

(2) Inhibition studies of the ethanol systems 103

Page

IV DISCUSSION

(A) Cyclohexane and its Binary Solutions 109

(a) Pure cyclohexane 109

(b) Inhibition experiments 118

(B) Radiolyses of Benzene, Cyclohexene and Propylene 139

(a) Benzene 140

(b) Cyclohexene 142

(c) Propylene 149

(C) Methyl Cyclohexane and its Binary Solutions 150

(a) Pure methyl cyclohexane 150

(b) Inhibition experiments 151

(D) Ethanol and its Binary Solutions 162

(a) Pure ethanol 162

(b) Inhibition experiments 172

(E) Summary of the Values of Ratios of Rate Constants in the Various Systems 180

BIBLIOGRAPHY 188

LIST OF TABLES

Table No.	Title	Page
I	The Columns and Conditions used for the Analyses of Liquid Products	57
II (a)	Pressure - Peak Height Data for Hydrogen and Methane	61
II (b)	Pressure - Peak Height Data for Hydrogen, Carbon monoxide and Methane	62
III	Calibration Factors of Gases Non-condensable at -112°C	66
IV	Calibration Factors for the Various Hydrocarbons Obtained in Cyclohexane Radiolysis	67
V	Calibration Factors of the Various Liquid Products	69
VI	Yield of Gas Volatile at -196°C as a Function of Volume of Liquid Cyclohexane Vapourised into the Reaction Chamber	73
VII	Yields of the Gases Volatile at -196°C and -112°C as a Function of Dose in the Radiolysis of Cyclohexane	76
VIII	G (Products) of Irradiation of Cyclohexane Vapour as a Function of Dose	78
IX	Gaseous Yields from the Irradiation of Cyclohexane - Benzene Solutions	81
X	Gaseous Yields from the Irradiation of Cyclohexane - Cyclohexene Solutions	82
XI	Gaseous Yields from the Irradiation of Cyclohexane - Propylene Mixtures	83

Table No.	Title	Page
XII	Electron Density Values for the Compounds used in the present work	85
XIII	G Values of Gaseous Products Obtained in the Radiolyses of Benzene and Cyclohexene Vapours and of Propylene	88
XIV	G Values of Products from the Vapour Phase Radiolyses of Benzene, Cyclohexene and Propylene	89
XV	Yields of Gases Volatile at -196°C and -112°C as a Function of Dose in the Radiolysis of Methyl Cyclohexane	91
XVI	Gaseous Yields from the Irradiation of Methyl Cyclohexane - Benzene Systems	94
XVII	Gaseous Yields from the Irradiation of Methyl Cyclohexane - Cyclohexene Systems	95
XVIII	Yields of Gases Volatile at -196°C and -112°C as a Function of Dose in the Radiolysis of Ethanol	99
XIX	G Values of Gases Volatile at -196°C and -112°C as a Function of Dose	101
XX	G Values of the Various Products Obtained by Irradiating Ethanol	104
XXI	Gaseous Yields from the Irradiation of the Ethanol - Benzene Systems	105
XXII	Gaseous Yields from the Irradiation of Ethanol - Cyclohexene Systems	106
XXIII	Material Balance of Products from Irradiation of Cyclohexane Vapour	112

Table No.	Title	Page
XXIV	Data for The Curve Fitting the Hydrogen Yield in Cyclohexane - Benzene Systems	125
XXV	Data for the Curve Fitting the Hydrogen Yield in Cyclohexane - Cyclohexene Systems	126
XXVI	Data for the Curve Fitting the Hydrogen Yield in Cyclohexane - Propylene Systems	127
XXVII	Values of Rate Constant Ratios Obtained from Mechanism (1)	129
XXVIII	Data for the Curve Fitting the Hydrogen Yield in Cyclohexane - Benzene Systems	133
XXIX	Data for the Curve Fitting the Hydrogen Yield in Cyclohexane - Cyclohexene Systems	134
XXX	Data for the Curve Fitting the Hydrogen Yield in Cyclohexane - Propylene Systems	135
XXXI	Value of Kinetic Parameters obtained from Mechanism (2)	137
XXXII	G Values and Material Balance of Products from Irradiation of Benzene Vapour	141
XXXIII	Material Balance and G Values of Products Obtained in the Radiolysis of Cyclohexene Vapour	144
XXXIV	Rate Constants at 108^{o}C for Hydrogen Abstraction Calculated from the Kinetic Parameters in References Cited	148
XXXV	Data for the Curve Fitting the (-196^{o}C) Fraction Yield in Methyl Cyclohexane - Benzene Systems	153

Table No.	Title	Page
XXXVI	Data for the Curve Fitting the (-196°C) Fraction Yield in Methyl Cyclohexane - Cyclohexene Systems	154
XXXVII	Values of Rate Constant Ratios Obtained from Scavenging Mechanism	156
XXXVIII	Data for the Curve Fitting the (-196°C) Fraction Yield in Methyl Cyclohexane - Benzene Systems	158
XXXIX	Data for the Curve Fitting the (-196°C) Fraction Yield in Methyl Cyclohexane - Cyclohexene Systems	159
XL	Values of Kinetic Parameters Obtained from Energy Transfer Mechanism	161
XLI	Mass Balance of Carbon, Hydrogen and Oxygen in the Various Products Obtained in the Radiolysis of Ethanol Vapour	166
XLII	Data for the Curve Fitting the (-196°C) Fraction Yield in Ethanol - Benzene Systems	175
XLIII	Data for the Curve Fitting the (-196°C) Fraction Yield in Ethanol - Cyclohexene Systems	176
XLIV	Values of Rate Constant Ratios Obtained from Scavenging Mechanism	178
XLV	Data for the Curve Fitting the (-196°C) Fraction Yield in Ethanol - Benzene Systems	182
XLVI	Data for the Curve Fitting the (-196°C) Fraction Yield in Ethanol - Cyclohexene Systems	183

Table No.	Title	Page
XLVII	Values of Kinetic Parameters Obtained from Energy Transfer Mechanism	185
XLVIII	Summary of Values of Kinetic Parameters Obtained from Scavenging mechanism in the Various Systems	186
XLIX	Summary of Values of Kinetic Parameters Obtained from Energy Transfer Mechanism in the Various Systems	187

LIST OF FIGURES

Figure No.	Title	Page
1	Main Manifold	46
2	Auxiliary Manifold	48
3	Hydrogen Calibration Curve	64
4	Methane and Carbon monoxide Calibrations	65
5	Calibration Curves used to Estimate the Correct Dose and Yield	70
6	Yield of Gas Volatile at -196°C as a Function of the Volume of Cyclohexane Liquid Vapourised	74
7	G(-196°C)and G(-112°C) as a Function of Dose	77
8	Product Yield as a Function of Dose	79
9	Hydrogen Yield as a Function of Protector Concentration	86
10	G(-196°C) and G(-112°C) as a Function of Dose	92
11	G(-196°C) as a Function of Protector Concentration	96
12	G(-196°C) and G(-112°C) as a Function of Dose	100
13	G Values of Products Volatile at -196°C and -112°C in the dose Function Experiments of Ethanol	102
14	G(-196°C) as a Function of Protector Concentration	107
15	Kinetic Plots of Scavenging Mechanism	128

Figure No.	Title	Page
16	Kinetic Plots of Energy Transfer Mechanism	136
17	Kinetic Plots of Scavenging Mechanism	155
18	Kinetic Plots of Energy Transfer Mechanism	160
19	Kinetic Plots of Scavenging Mechanism	177
20	Kinetic Plots of Energy Transfer Mechanism	184

I INTRODUCTION

General

Because of the large volume of literature which has been published in radiation chemistry, and the wide scope of the present investigation, the introduction has been divided into five distinct sections. Each section is a review, though not critical, of the available literature deemed pertinent to the present investigation. The first section is a historical survey of the development of radiation chemistry in general. In the second section, concepts of mechanisms in radiation chemistry are discussed. A survey of the previous studies of the radiolysis of the compounds used in the present work constitutes the third part. The various methods of measuring the dose absorbed by an irradiated system are reviewed in the fourth part. The scope of the present investigations constitutes the final section of the introduction.

(A) Historical

Radiation chemistry is defined as the study of the chemical effects caused by ionising radiations in their passage through matter. The first such study, reported in 1896 by Becquerel (1), concerned the action of

radiation emitted by uranium on a photographic plate. Radiation chemistry, however, is still in its infancy. This is particularly true with respect to organic compounds. The approach to the subject was often empirical. At present, with the greater availability of radioactive elements and particle accelerating machines, the study of radiation chemical effects on compounds is being actively pursued.

The first systematic approach to the study of the effect of ionising radiations was made by Lind (2). Most of his studies were confined to the effects of radon alpha rays on gaseous hydrocarbons. Modern studies are extended to the effects of other charged particles such as protons, accelerated helium ions, electrons and deuterons, and of electromagnetic radiations such as x-rays and -rays. Neutral particles such as neutrons and neutrinos have relatively small effect because they do not cause primary ionisation. Lind, through his experimental work, concluded that ions were the major chemically reactive species produced during the irradiations and that these ions were the precursor of the observed chemical effects. The observed chemical effects were thought to depend on the nature and the stability of these ions in their environment. Attempts were then made to determine

the nature of the general environment surrounding these ions. In one such experiment, it was found that the small mobility of the gaseous ions could not be satisfactorily explained by simple kinetic theory, assuming ordinary molecular diameters (3). To circumvent this difficulty, it was suggested that the small mobility might be due to an entity with a larger diameter than that of the ordinary molecules. These entities were postulated to consist of a cluster of neutral molecules around a central ion held thereto by strong polarization forces. The low mobility was then ascribed to a drag exerted on the ions by dipole forces set up in the molecules past which they drift (3).

The idea of the formation of clusters was independently conceived by Lind (2) and Mund (4) to explain the radiation chemical reactions. Lind expressed his experimental yields in terms of "ionic yield". The ionic yield, expressed as M/N, the number of molecules formed or destroyed per ion pair produced, was considered as the radiation chemical analogue of the photochemical quantum yield. When he noticed that the ionic yield exceeded unity, he put forward the "cluster hypothesis". In this hypothesis, it was postulated that several molecules clustered around each ion; the breakdown of such clusters occurred when they were neutralised by an ion or cluster of opposite charge;

then the molecules in the cluster shared the heat of neutralisation to undergo reaction. Thus the rate of reaction would sometimes be greater than the rate of production of ions. Although the "cluster hypothesis" successfully explained some of the experimental results, some major difficulties were encountered in accepting the hypothesis as a general mechanism for radiation chemical reactions. Firstly, the theoretical work of Eyring et al (5) showed the improbability of the formation of clusters in the reaction systems investigated. In addition, it was found that free radical mechanisms were capable of explaining the observed results. Secondly, Essex and his co-workers (6-9) showed that the reaction rates were not reduced to zero in several systems even when the ionic concentration was reduced to a negligible extent by the application of high potentials. This illustrated that a considerable fraction of reaction was quite independent of the production of ions which were the centres of formation of the clusters. Thirdly, the excess energy in a reaction (W-I, where W represents the average energy expended per ion pair produced and is $\simeq$ 26-38 ev and I is the ionisation potential $\simeq$ 9-15 ev) could be used to form chemically reactive species other than ions.

The above mentioned reasons demonstrate the

fact that cluster formation is not the sole cause of the observed radiation chemical effects; but they do not deny the existence of weakly held clusters (with the energy attachment of the order of thermal motion). The present trend is to accept the formation of free radicals and excited molecules but not to ignore the possible effect of cluster formation.

The experimental results in radiation-induced reactions were usually expressed as ionic yields (M/N). This method of expressing the radiation chemical yields has been replaced by the "G" value (10). "G" is the number of molecules produced or destroyed per 100 ev of energy absorbed. The replacement of M/N by G has several advantages:

(1) the number of ion-pairs, N, is not and probably can never be, experimentally known in condensed systems (11).

(2) the mechanisms are not always determined by ionic reactions and there is no reason for expecting excited molecules to be generally ineffective.

(3) radical chain reactions do not permit a simple interpretation of M/N.

The nature of the chemical processes in radiation chemistry and photochemistry are similar in that

they both contain free radical processes. In photochemistry the photon is completely absorbed in a single molecule and a well defined excited state is formed. In radiation chemistry, the energy of a fast particle is slowly dissipated during its passage through matter and the number of excited molecules and ions formed is proportional to the initial energy of the particle.

A photochemical reaction is a three step process:

(1) absorption of light resulting in the production of excited molecules.

(2) the excited molecules either decompose or react to give products which may be final products or atoms or radicals.

(3) if atoms or radicals are produced, they undergo a further reaction to give ultimate products.

The primary processes in radiation chemistry involve both ionisation and excitation. The fact that these are two distinct and simultaneous primary processes complicates matters considerably. The ionised and excited molecules are concentrated along the path of the high energy particle. These ionised and excited molecules are more likely to react with their immediate neighbours than with similar species from other tracks ("Track effect", (12)). This is more likely to occur in condensed than in gaseous media.

The amount of ionisation and excitation per unit path length (the ionisation and excitation density) is mainly dependent on the velocity and mass of the ionising particles. Heavy, relatively slow moving radiations, such as alpha particles, produce continuous tracks or columns of ionisation and excitation. High speed electrons produce relatively widely separated "spurs" or "hot spots" of reactive fragments. Ionisation and excitation density of the tracks, as well as diffusion and cage effects might play a major role in determining the types and yields of stable products in condensed media.

(B) Concepts of Mechanisms in Radiation Chemistry

(a) Absorption and migration of energy

All ionising radiations transfer at least a part of their energy to an irradiated system. The amount of energy absorbed by a molecule is dependent on its distance from the passing ionising radiation. If the energy absorbed is greater than the ionisation potential of the molecule, an electron is ejected resulting in ionisation. If the energy absorbed is less than the ionisation potential, an extranuclear electron may merely be raised to an excited level. The variety of transitions to different levels of excitation will then depend on the

proximity between the molecule and the ionising radiation and upon the nature of the interaction between the radiation and the molecules.

Although the excited states permissible by optically allowed transitions are the ones often formed, optically forbidden excited states are known to be formed by the effect of slow electrons (energy 20 - 100 ev) (13). Since most molecules are in singlet states, excitation to singlet states is most probable, although excitation to triplet states can also be expected (14). Experimental information about excitation of singlet to triplet states in a large variety of organic molecules has been summarised by Mc Lure (15). The emission lifetimes of the meta-stable triplet states were found to be in the range from 10^{-4} to about 10 seconds. Besides the major effects of excitation and ionisation, there are other negligible effects arising from nuclear collisions, such as auger disruptions and multiple ionisations when neutrons impinge on molecules containing hydrogen atoms (16).

After the formation of primary ions and excited molecules, a number of secondary processes may ensue prior to the occurrence of the final chemical change. Such processes might include transfer of excitation energy and ionisation, formation of negative ions and neutralisation of

ions. These processes are part of the means of dissipation of the absorbed energy in the system. Some of the excitation transfer and migration processes have been reviewed by Laidler and Schuler (17).

(1) Transfer of excitation energy

To the present, the most informative studies on excitation transfer have arisen from scintillation experiments in solids and in liquid solutions of suitable organic compounds, under the influence of ionising radiation. In these experiments (18 - 23), the energy is absorbed by the major compound and is liberated in the form of fluorescence of the minor component. Four mechanisms have been proposed for this migration of energy. They are:

(i) sensitised fluorescence:- This phenomenon was first observed in gases and Forster (24) later developed a quantum-mechanical theory to explain it. This theory was supported by experiments on dye solutions. In this theory, the energy is assumed to be transferred by quantum-mechanical resonance from a solvent molecule to a distant solute molecule, molecules in between playing no part in the transfer.

(ii) exciton transfer:- This concept originated from work on energy transport in crystals. In this concept, the energy is transferred from molecule to molecule and the energy remains in any molecule for less time than a period

of one vibration. Livingston (25) has discussed the significance of exciton migration. For the process of exciton migration to occur, Franck and Livingston (26) think that a strong coupling is necessary.

Birks (27) examined the mechanism of energy transfer from excited solvent to solute molecules and concluded that both the sensitised fluorescence and the exciton concept are inadequate to explain the mechanism of energy transfer because both require a degree of electronic coupling which may not exist in organic systems.

Burton and Patrick (28) suggest that only excitation transfer and not charge transfer is relevent to radiation chemistry. However this has met some opposition (29) and experiments have indicated that an electron capture might play a major role in some radiation processes (30).

(iii) photon transport:- This theory assumes that the radiation emitted by a solvent molecule is ultimately absorbed by a solute molecule which then emits its own characteristic radiation (21).

(iv) photon cascade:- This concept postulates that fluorescence is emitted by a solvent molecule in transition from higher excited states to the first excited state. The time taken for such transitions is very small (

10^{-11} to 10^{-12} seconds). The emitted radiation is absorbed by neighbouring solvent molecules and the process is repeated until all the molecules reach the first excited state. The normal fluorescence emitted by the solvent molecules is then absorbed by the solute molecules. Then these solute molecules emit their own fluorescent radiation.

Collinson and Swallow (as in Ref.24) state that the present position seems to be one in which sensitised fluorescence is rejected and photon transfer, though it occurs, is trivial; while it is still difficult to decide between the photon cascade and the exciton mechanisms, the former seems to be more acceptable.

(2) Ionisation transfer

Alternatively this is referred to as charge transfer, and it involves the transfer of an electron. There are two mechanisms proposed for the transfer of a single charge in gas phase collisions.

(i) the resonant process:- This process is represented by

$$A^+ + A \longrightarrow A + A^+$$

This process may have a large cross-section since the momenta of the pair (ion and molecule) do not have to change as the electron jump occurs and a close collision is not necessary (31).

(11) the non-resonant process:- This process is represented by

$$A^+ + B \longrightarrow A + B^+$$

This is analogous to a quenching reaction. For the non-resonant charge transfer to occur, the two potential curves of the system must cross (31,32). Since the potential curves contain the vibrational energy of the system, the charge transfer is usually accompanied by vibrational excitation.

There are two kinds of non-resonant processes, the adiabatic and the non-adiabatic. In the adiabatic non-resonant charge transfer, dissociation of one of the molecules occurs:

$$A^+ + B \longrightarrow B^+ + C + D$$

In non-adiabatic charge transfer, the system changes from one excitation state to another without chemical transformation.

(3) Electron capture

Magee and Burton (33) have discussed the theory of electron capture by molecules. In an irradiated system, primarily, electrons, positive ions and neutral molecules prevail. The neutralisation of positive ions or the formations of negative ions is determined by the degree of competition between neutral molecules and positive ions in

electron capture.

(i) neutralisation of positive ions:- The electron knocked out of the neutral atom or molecule during irradiation, moves back into its hole and thus neutralises the ion. The heat of neutralisation manifests itself in the form of excitation energy. As a result of neutralisation of the ions, excited molecules are created and the energy might be dissipated through chemical reaction or as heat.

(ii) formation of negative ions:- Low energy electrons (1/3 ev in gases, 1/4 ev in liquids (33)) sometimes disappear by forming negative ions with neutral molecules rather than by neutralisation of positive ions. Common substances which give negative ions by thermal electron capture are oxygen, water, alcohols, alkyl halides and in general all compounds in states in which they have low lying vacant orbitals. For capture of thermal electrons in a dissociative process, the electron affinity of the ion produced must be greater than the strength of the bond ruptured. Such processes tend to increase the ion pair yield. Williams and Essex (8) have reported an increase in the ion yield by negative ion formation during the alpha irradiation of nitrous oxide.

(b) General mechanisms of radiolysis

Several general mechanisms by which radiolytic

processes may take place can be found in the literature. The current trend of interpreting product formation during radiolysis by free radical mechanisms and ion molecule reactions is also included.

(1) Cluster mechanism

Gas phase studies such as oxidation, hydrogenation, decomposition and polymerisation of various hydrocarbons were performed by Lind (2). In these experiments, substances in the vapour phase were mixed with radon and the latter was allowed to decay before the mixtures were analysed. The initial phases of the reactions were not observed in these systems. Lind explained the mechanism of these reactions by the formation of clusters. His cluster mechanism has been found to be inadequate to explain the varied aspects of radiation chemistry developed in recent years and hence it is only of historical importance. Recently Magee and Funabashi (34) have attempted to calculate the importance of clustering in gases.

(2) Burton's mechanism

A mechanism of induction of chemical change in gases exposed to ionising radiation has been presented by Burton (35) based on the experiment and theory of Eyring, Hirschfelder and Taylor (5). The ionisation process is schematically represented as

$$A \rightsquigarrow A^{+} + e \qquad \text{--(1)}$$

Here A is a reactant molecule and A^{+} is the molecule-ion. The ejected electron may undergo two possible reactions:

(i) The electron may combine with A^{+} and result in an excited molecule

$$A^{+} + e \longrightarrow A^{*} \qquad \text{--(2)}$$

A knowledge of photochemistry indicates that the possible fates of this excited molecule are

A^{*} → bonds might break to form radicals --(3)

A^{*} → rearrangement to give ultimate products --(4)

(ii) The other possibility for the disappearance of this electron may be in the formation of a negative ion.

$$M + e \longrightarrow M^{-} \qquad \text{--(5)}$$

M and A may be identical. The stability of M^{-} depends on its life period before neutralisation and the various potential energy relations inside the whole system. Possible ways in which M^{-} might disappear are:

$$M^{-} \longrightarrow R + X^{-} \qquad \text{--(6)}$$

$A^+ + M^- \longrightarrow$ characteristic reaction --(7)

For about twenty years, Essex and coworkers have investigated gas phase radiolysis reactions and as a result Essex (36) has indicated that such reactions are initiated by several mechanisms. The mechanisms suggested by Essex are semi-quantitative treatments of the above mechanisms (1) and (2).

(3) Free radical mechanism

It is becoming more and more evident that the radiolytic decomposition of organic systems proceeds partly by free radical mechanism. By the use of reactive solutes as scavengers, the free radical yields have been estimated. More will be said about free radical scavenger studies elsewhere in the thesis. Information concerning free radical reactions is available in the literature from photochemical studies (37).

(4) Ion-molecule reactions

It was thought for many years that ions formed in the primary process merely underwent neutralisation, thus resulting in excited species and free radicals. In recent years, however, mass spectrometric investigations (38 - 40) have disclosed many extremely rapid reactions between ions and molecules in the gas phase. These reactions occur so rapidly that they appear capable of

competing favourably with neutralisation reactions. Reactions of the following type might occur in radiolytic systems:

$$M \longrightarrow M^+ + e \qquad \text{--(1)}$$

$$M^+ + e \longrightarrow M \qquad \text{--(2)}$$

$$M^+ \longrightarrow F^+ + G \qquad \text{--(3)}$$

$$M^+ (F^+) + M (N) \longrightarrow P^+ + Q \qquad \text{--(4)}$$

Here M and N are reactant molecules; F^+ and P^+ are intermediate ions; G and Q are free radicals.

According to Stevenson (41), reaction (4) (ion-molecule type) at atmospheric pressure and reasonable dose rates occurs much faster than the neutralisation reaction(2). Mass spectrometric experiments (38 - 40) provide evidence in support of this view. Irradiation reactions in hydrocarbon gases studied by Lampe (42) have clearly demonstrated the importance of ion-molecule reactions in radiation chemistry.

(c) Inhibition mechanisms

To isolate steps in radiolytic mechanisms, the study of binary systems, particularly of pairs of compounds which differ only slightly in properties, should be very helpful. Such studies were made in cyclohexane-benzene and

cyclohexane-cyclohexene systems by Burton and coworkers (28, 43,44).

It is well known that the product yields in the radiolysis of some organic systems can be markedly reduced by addition of small amounts of certain substances. Several mechanisms can be invoked to explain such effects. These can be broadly classified into (1) a scavenger effect, where the additives combine with the free radicals produced from excited and ionised molecules, and (2) an energy-transfer protection effect where the additives effect the precursors of the first chemical decomposition. In the protection effect, the additive appears to provide an alternate path for energy dissipation, e.g., by inducing internal conversion in the excited solvent to a lower excited state which then dissipates its electronic energy as heat (45), by excitation transfer to the additive or by negative ion formation. Scavenging and protection effects will be dealt with separately.

(1) Scavenger studies

Reactive solutes, used as scavengers, trap the free radicals as they are formed, thereby eliminating their contribution to the decomposition products. From such studies, it has been possible to obtain information about the free radical processes. One such reactive solute very

often used is iodine (46 - 53). Radioisotope I^{131} has been very effectively employed for the identification of small amounts of products in the cases of hydrocarbon vapours (54) and liquid butane (48). Iodine appeared to have little effect on hydrogen production in case of cyclohexane if its concentration was below 10^{-3} M (47). Schuler (47) concluded that the lack of effect at low concentrations makes it seem evident that the presence of solutes at low concentrations does not affect the nature of the primary chemical processes. However at higher concentrations its presence reduced the yield of hydrogen (47,55). In general, to study scavenging, the choice of concentration of the scavenger should be carefully made. If too high a concentration of the scavenger is employed, a misleading picture regarding the processes might be conceived because of the direct radiolysis of the scavenger. Recent work by Mc Cauley and Schuler (48) on the reaction between iodine and liquid butane is an illustration of this fact. In this investigation, contrary to expectation, they obtained a large increase in the yield of high boiling iodides at concentrations above 10^{-2} M iodine.

Since higher concentrations of reactive solutes introduce complications and thus limit scavenger studies to low solute concentrations, the activation energy for the scavenging reaction must be considerably lower than those

for other possible reactions of free radicals. In hydrocarbon systems, consideration of competition between scavenging and possible hydrogen abstraction is important. If in a system, scavenging is faster, reaction (1) must predominate over reaction (2).

$$R\cdot + S \longrightarrow RS \qquad \text{--(1)}$$

$$R\cdot + R'H \longrightarrow RH + R' \qquad \text{--(2)}$$

Here S represents a scavenger.

Since the activation energy for the abstraction reaction is itself low ($\simeq$ 8 K. cals/mole) (37), the scavenging reaction must have a considerably lower activation energy. The evidence from the work of Melville and Robb (56) is that it has zero activation energy for benzene and cyclohexene, at least in the gas phase.

(2) Protection studies

Cyclohexane-benzene systems, in which the production of hydrogen decreased due to the presence of benzene, have been investigated (28,43,44,57,58). Instances where cyclohexene acts as a protector to cyclohexane have also been studied (43,57,61). Based on various other investigations, as well as their own, Burton and Lipsky (55) have suggested several possible mechanisms of protection. These are:

(i) energy transfer or sponge type protection mechanism:- If the protector has an ionisation potential or excitation potential lower than that of the solvent, energy transfer from solvent to the protector may occur either via transfer of a virtual photon or by charge transfer. The probability of energy transfer by photon emission depends upon whether it can occur before the processes of rupture and rearrangement. In condensed systems, there is more likelihood of a series of resonant ionisation transfers from solvent molecule to solvent molecule until the charge can be trapped by the additive (62).

(ii) quenching mechanism:- The solute might promote the distribution of the initially localised energy among vibrational and rotational degrees of freedom of neighbouring solvent molecules. For quenching to be efficient, the interaction between the quencher and the excited molecule must compete effectively with the rapid rupture and rearrangement processes. It has been found that certain quenchers may depopulate the excited states of scintillation solvents at rates perhaps a hundred times greater than the rates of radiation emission (63).

(iii) negative ion formation mechanism:- Excited molecules may be formed either by an electron moving into its positive hole or by combination of a positive and a

negative ion.

$$M^+ + e \longrightarrow M_1^* \qquad --(1)$$

$$M^+ + N^- \longrightarrow M_2^* \quad N \qquad --(2)$$

The excited states resulting from reaction (1) are in general higher than those resulting from reaction (2)(55). If reaction (2) becomes the predominant source of excited molecules, the chemistry of the subsequent processes may be greatly modified; e.g., rearrangement may become the only decomposition process or, perhaps, only metathetical reactions of the excited molecules may occur or decomposition may be entirely prevented.

(iv) ion molecule reactions:- When an additive (e.g., B) can capture the ionisation before neutralisation can occur

$$M^+ + B \longrightarrow M + B^+$$

the following neutralisation reaction involves B^+ and M is thus protected against decomposition.

(C) Survey of Previous Studies of the Radiolysis of the Compounds used in the Present Work

(a) Cyclohexane

The radiolysis of liquid cyclohexane has been

investigated by using alpha particles (59), electrons (28, 43,57,59,60,64,65,66), γ -rays (47,53,58,61,64,67-71), and X-rays (46,72). Hydrogen was the major single product in all cases. Among the few studies that have approached the problem kinetically, works of Manion and Burton (43), Burton and Patrick (28), and Freeman (58) are noteworthy. The investigations of Manion and Burton (43), Dewhurst(66), and Freeman (58) are pertinent to the development of this thesis and will be briefly described here.

Although in two of these investigations (43,58), the radiolysis of pure liquid cyclohexane has been investigated, the studies are diverted to the protection of cyclohexane by benzene and cyclohexene.

Pure cyclohexane was irradiated both in the liquid and the vapour phase by Manion and Burton (43), using electrons. The gaseous products fractionated at -196°C consisted of hydrogen and methane and the -120°C fraction consisted of ethane, ethylene and acetylene. The amount of polymers formed were estimated by allowing the irradiated liquid to evaporate to constant weight. They obtained G (H_2) = 5.7, G (CH_4) = 0.09, G (C_2 total) = 0.21, G (Polymer) = 1.7 in the liquid phase and G (H_2) = 1.4, G (CH_4) = 0.07, G (C_2H_4) = 0.31, G (C_2H_6) = 0.17 in the vapour phase radiolysis. The addition of benzene or cyclohexene to

the cyclohexane caused the yields of the gaseous products to decrease. The decreased yield was attributed to a "Sponge type" protection. A mechanism for the pure cyclohexane radiolysis in the vapour phase was also indicated.

From the ratio of G (C_2H_4) to G (C_2H_6) equal to 1.8 obtained during the vapour phase radiolysis, Manion and Burton suggested that these products were formed by a ring opening reaction followed by "unpeeling".

$$C_6H_{12} + H \longrightarrow -(CH_2)_5 - CH_3 \qquad --(1)$$

$$\downarrow$$

$$C_2H_4 + -(CH_2)_3 - CH_3 \qquad --(2)$$

$$\downarrow$$

$$C_2H_4 + -C_2H_5 \qquad --(3)$$

The ethyl radical ultimately was assumed to yield ethane either by combination with a free H atom or by reaction with a hydrogen molecule. They postulated that the hydrogen atom involved in reaction (1) was probably hot so that reactions (1) to (3) were reasonable.

Dewhurst (66) analysed the products of liquid cyclohexane radiolysis and found a linear C_6 hydrocarbon (hexene), methyl cyclopentane, cyclohexene, intermediate

cyclohexanes, dicyclohexyl and cyclohexyl-cyclohexene. But the only measured yields were G (cyclohexene) = 2.5 and G (dicyclohexyl) = 2.0. The major products formed in the radiolysis of liquid cyclohexane were attributed to C - H bond scission without the rupture of the ring. The minor products were ascribed to the fragmentation and isomerisation of the ring system.

Pure liquid cyclohexane and systems consisting of mixtures of cyclohexane-benzene (58) and cyclohexane-cyclohexene (61) were also studied by Freeman, using Co^{60} γ-rays. The conclusion that at least two chemically active species of cyclohexane exist was reached. Of the two active species, one, designated by $c\text{-}C_6H_{12}$" was protected by benzene (or cyclohexene) and the other was not. The approximate yields of these two active species, as determined by kinetic analysis, were G ($c\text{-}C_6H_{12}$") = 3.0 ± 0.4 and G ($c\text{-}C_6H_{12}$') = 2.4 ∓ 0.4. In the cyclohexane-benzene system, in addition to the usual products, cyclohexyl-cyclohexadiene and dicyclohexadiene were reported. A mechanism consistent with the product yields was given and is mentioned below.

$$c\text{-}C_6H_{12} \xrightarrow{I} c\text{-}C_6H_{12}^{*} \qquad \text{--(1)}$$

$$C_6H_6 \xrightarrow{I} C_6H_6^{*} \longrightarrow \text{products} \qquad \text{--(2)}$$

$$c\text{-}C_6H_{12}^{*} + C_6H_6 \longrightarrow c\text{-}C_6H_{12} + C_6H_6 \qquad \text{--(3)}$$

$$c\text{-}C_6H_{12}^{*} \longrightarrow c\text{-}C_6H_{11} + H \qquad \text{--(4)}$$

$$H + c\text{-}C_6H_{12} \longrightarrow H_2 + c\text{-}C_6H_{11} \qquad \text{--(5)}$$

$$H + C_6H_6 \longrightarrow C_6H_7 \qquad \text{--(6)}$$

By kinetic treatment, Freeman found that the effects were split into two quite distinct benzene concentration regions. At low benzene concentrations rapid scavenging occurred with a certain fraction of the hydrogen atoms. At higher benzene concentrations energy transfer protection seemed also to occur. Since the total yield of cyclohexadiene polymers were found to be directly proportional to the electron fraction of cyclohexane, the following reactions were suggested. The reactions

$$c\text{-}C_6H_{12}' \longrightarrow c\text{-}C_6H_{11} + H \qquad \text{--(4')}$$

and

$$H + C_6H_6 \longrightarrow C_6H_7 \qquad \text{--(6)}$$

occur rapidly by comparison with

$$c\text{-}C_6H_{12}' + C_6H_6 \longrightarrow c\text{-}C_6H_{12} + C_6H_6 \qquad \text{--(3')}$$

and

$$H + c\text{-}C_6H_{12} \longrightarrow H_2 + c\text{-}C_6H_{11} \qquad \text{--(5)}$$

where $c\text{-}C_6H_{12}'$ represents a particular activated species

of cyclohexane. For another excited species $c\text{-}C_6H_{12}''$, the reaction

$$c\text{-}C_6H_{12}'' + C_6H_6 \longrightarrow c\text{-}C_6H_{12} + C_6H_6 \qquad --(3'')$$

is sufficiently rapid that it may compete with

$$c\text{-}C_6H_{12}'' \longrightarrow c\text{-}C_6H_{11} + H \qquad --(4'')$$

The heavy radicals react as follows:

$$2\ c\text{-}C_6H_{11} \longrightarrow (c\text{-}C_6H_{11})_2 \qquad --(7a)$$

$$\longrightarrow c\text{-}C_6H_{10} + c\text{-}C_6H_{12} \qquad --(7b)$$

$$c\text{-}C_6H_{11} + c\text{-}C_6H_7 \longrightarrow c\text{-}C_6H_{11} - C_6H_7 \qquad --(8a)$$

(cyclohexyl-cyclohexadiene)

$$\longrightarrow c\text{-}C_6H_{10} + c\text{-}C_6H_8 \qquad --(8b)$$

(cyclohexadiene)

$$\longrightarrow c\text{-}C_6H_{12} + C_6H_6 \qquad --(8c)$$

$$2\ c\text{-}C_6H_7 \longrightarrow (c\text{-}C_6H_7)_2 \qquad --(9a)$$

(dicyclohexadiene)

$$\longrightarrow C_6H_6 + c\text{-}C_6H_8 \qquad --(9b)$$

Cyclohexyl hexene, one of the products detected, was suggested to be formed by the reactions

$$c\text{-}C_6H_{12}^{iv} \longrightarrow c\text{-}C_6H_{11}^{*} + H \qquad \text{--(10)}$$

$$c\text{-}C_6H_{11} \longrightarrow CH_2 = CHCH_2CH_2CH_2CH_2 \qquad \text{--(11)}$$

$$CH_2{=}CH(CH_2)_4 + c\text{-}C_6H_{11} \longrightarrow c\text{-}C_6H_{11}(CH_2)_4\,CH{=}CH_2 \qquad \text{--(12)}$$

Due to the absence of a sudden large decrease in G (cyclohexyl hexene) at low benzene concentrations, Freeman classed $c\text{-}C_6H_{12}^{iv}$ along with $c\text{-}C_6H_{12}''$ species rather than with those represented by $c\text{-}C_6H_{12}'$.

Although liquid cyclohexane radiolysis has been vastly studied, there have been very few investigations of cyclohexane vapour (43,73). Henri and coworkers (73) irradiated several C_6 hydrocarbons with radon alpha particles. They suggested that the parent hydrocarbon underwent excitation and ionisation followed by rupture of the molecule into two or more ions or free radicals. These fragments then recombine, on primarily a statistical basis, until all the electrical charges and free valence bonds were neutralised.

(b) Cyclohexene

The radiolysis of cyclohexene vapour by radon alpha particles has been investigated by Henri et al (73). The major products obtained were hydrogen (G = 1.07), ethylene (G 1.30), acetylene (G = 0.49), methane (G = 0.27) and propylene (G = 0.19) with minor amounts of benzene (G = 0.07),

C_4 hydrocarbons (G = 0.05), ethane (G = 0.04) and propane (G = 0.02). The mechanism of decomposition was discussed in a general way.

An investigation of the γ-radiolysis of liquid cyclohexene, with a fairly complete analysis of the products, was made by Freeman (61). The detected products and their G values mentioned in parenthesis were as follows: hydrogen (1.2), ethylene (0.16), acetylene (0.022), C_4 hydrocarbon(0.10), cyclohexane (1.0), dicyclohexenyl (1.36), cyclohexyl cyclohexene (0.22), dicyclohexyl (0.11), total C_{12} hydrocarbons (1.96) and total polymer (8 cyclohexene units). The term "polymer" includes the C_{12} hydrocarbons. The formation of the major identified products was explained by the following mechanism:

$$c\text{-}C_6H_{10} \xrightarrow{I^*} c\text{-}C_6H_{10}^* \qquad \text{--(1)}$$

$$\xrightarrow{I^{**}} c\text{-}C_6H_{10}^{**} \qquad \text{--(1a)}$$

$$c\text{-}C_6H_{10}^* \longrightarrow c\text{-}C_6H_9 + \text{cold H} \qquad \text{--(2)}$$

$$c\text{-}C_6H_{10}^{**} \longrightarrow c\text{-}C_6H_9 + \text{hot H} \qquad \text{--(2a)}$$

$$\text{hot H} + c\text{-}C_6H_{10} \longrightarrow H_2 + c\text{-}C_6H_9 \qquad \text{--(3)}$$

$$\text{cold H} + c\text{-}C_6H_{10} \longrightarrow c\text{-}C_6H_{11} \qquad \text{--(4)}$$

$$c\text{-}C_6H_{11} + c\text{-}C_6H_{10} \longrightarrow c\text{-}C_6H_{12} + c\text{-}C_6H_9 \qquad \text{--(5)}$$

$$2\ c\text{-}C_6H_9 \longrightarrow (c\text{-}C_6H_9)_2 \quad \text{(dicyclohexenyl)} \qquad \text{--(6a)}$$

$$\longrightarrow c\text{-}C_6H_{10} + c\text{-}C_6H_8 \qquad \text{--(6b)}$$

$$c\text{-}C_6H_9 + c\text{-}C_6H_{11} \longrightarrow c\text{-}C_6H_9 - C_6H_{11} \quad \text{(cyclohexyl cyclohexene)} \qquad \text{--(7a)}$$

$$\longrightarrow c\text{-}C_6H_8 + c\text{-}C_6H_{12} \qquad \text{--(7b)}$$

$$\longrightarrow 2\ c\text{-}C_6H_{10} \qquad \text{--(7c)}$$

$$2\ c\text{-}C_6H_{11} \longrightarrow (c\text{-}C_6H_{11})_2 \quad \text{(dicyclohexyl)} \qquad \text{--(8a)}$$

$$\longrightarrow c\text{-}C_6H_{10} + c\text{-}C_6H_{12} \qquad \text{--(8b)}$$

Freeman postulated the existence of two active species of cyclohexene. One active species decomposed to "cold" H atoms and the other to "hot" hydrogen atoms. The cold H atoms added to the cyclohexene molecules and the hot H atoms abstracted from the cyclohexene. The formation of C_4 hydrocarbon (probably butadiene) was attributed to ring cleavage of cyclohexene. The value for the ratio $k_{7a}/(k_{8a}k_{6a})^{\frac{1}{2}}$ was found to be 0.45 ± 0.08.

(c) Benzene

Many workers have radiolytically investigated the decomposition of liquid benzene (43,44,58,76) and benzene

vapour (43,73-75). The 100 ev yields of hydrogen, $G(H_2)$, in the vapour phase are at variance and range from 0.011 (43) to 0.3 (73). Theoretically, Burton (as in Ref.74) predicts G (gas) to be $\simeq 2$ for benzene vapour.

A comparison of vapour and liquid benzene radiolyses has been made by Manion and Burton (43). Ethylene is not produced in the radiolysis of liquid benzene although it is produced with a yield of G $(C_2H_4) = 0.05$ from benzene vapour. A simple interpretation for the formation of low molecular weight straight chain hydrocarbons such as C_2H_2 and C_2H_4 was attempted. This interpretation was made on the basis of the work of Schiff and Steacie (77) and Scott and Steacie (78) where the formation of low molecular weight straight chain hydrocarbons was attributed to the cracking of the gaseous benzene by epithermal hydrogen atoms. Manion and Burton ascribe the production of acetylene and ethylene in the radiolysis of gaseous benzene to hot hydrogen atoms produced in the primary step. A hydrogen atom opens the benzene ring in accordance with reaction (1) and the opened ring unpeels by successive reactions (1a).

$$H + C_6H_6 \longrightarrow -C_6H_7 \qquad \text{--(1)}$$

$$-C_6H_7 \longrightarrow CH=CH + -C_4H_5 \qquad \text{--(1a)}$$

$$\downarrow$$

$$2\ CH=CH + -C_2H_3 \qquad \text{--(1a)}$$

The C_2H_3 ultimately captures a hydrogen atom to give C_2H_4. Alternatively, after the formation of $(-C_6H_7)$ by reaction (1), the formation of acetylene and ethylene might take place by the following reactions:

$$-C_6H_7 + H \longrightarrow C_6H_8$$

$$C_6H_8 \longrightarrow 2\ C_2H_2 + C_2H_4$$

The G values that they reported for the products were not absolute and hence are of only relative significance.

Henri et al (73) irradiated benzene vapour by radon alpha particles and found the following product yields: hydrogen (G = 0.3), methane (G = 0.01), acetylene (G = 0.42), ethylene (G = 0.02) and ethane (G = 0.006). No mechanism for the decomposition of benzene vapour was suggested.

(d) Propylene

The γ- radiolysis of propylene has been recently studied by Back (79). The gas yields from the vapour phase radiolysis of various hydrocarbons reported in two papers by Back (79,80) are not entirely self-consistent, but the value of G (H_2) $\simeq$ 1.3 - 2.4 can be calculated for propylene from his results.

(e) Methyl cyclohexane

There are only a few references made in the

literature to the radiolysis of methyl cyclohexane (57,72, 81). Schoepfle and Fellows (57) irradiated methyl cyclohexane by cathode ray bombardment during a comparative study of hydrocarbons. Only percentage yields of gases were measured. Liquid methyl cyclohexane radiolysis by Flanagan and coworkers (81) shows G (total gas)=4.5. Weber et al (72) have done scavenging studies by irradiating a solution of iodine in methyl cyclohexane with x-radiation. They studied iodine disappearance as a function of dose and molecules reacting per 100 ev of energy absorbed at several iodine concentrations. It was found that the rate of iodine disappearance was nearly independent of iodine concentration in the range 0.0001 M to 0.0006 M ($G(-I_2) = 3.1$). The disappearance of iodine was attributed to reaction with organic radicals and not to reaction with hydrogen atoms. In that study, the radical yield measured by the uptake of iodine, in the case of some hydrocarbons, $G(R) = 6.8$, was found to be in approximate agreement with the value, $G(R) = 7.0$, obtained by Chapiro et al (82,83) who used diphenyl picryl hydrazyl as the radical detector.

(f) Ethanol

In the radiolysis of organic compounds in general, the investigations of those with generic groups are

relatively few in number. Mc Lennan and Patrick (84) were the first to report the products from cathode ray bombardment of methyl and ethyl alcohol vapours. The products were hydrogen, carbon monoxide, carbon dioxide, methane in the case of methanol and ethane in the case of ethanol. In the non-gaseous products, formaldehyde and acetaldehyde were found, methyl alcohol favouring formaldehyde and ethyl alcohol favouring acetaldehyde formation. Mc Donell and Newton (85) irradiated a series of liquid alcohols with 28 Mev helium ions. From both these pioneer works, it was evident that hydrogen was the major single product, followed by glycols and aldehydes. Mc Donell and Newton concluded from their study that hydrogen was formed exclusively from the CH_2 group in the case of ethanol. The only alcohol that did not give hydrogen as the major single product was tertiary butyl alcohol (85). In this case more methane than hydrogen was produced. The reason attributed for greater production of methane in the case of tertiary butyl alcohol was that, since no alpha C-H bonds were present, the next most readily broken bonds were the alpha C-C bonds.

It is evident from the above that the bonds on the carbon alpha to the -OH group are the most easily ruptured. One explanation for this preferential rupture is

based on the concept of formation of trivalent oxygen, derived from mass-spectral experiments (86,87). It is assumed that, in the positive ethanol ion, the charge is localized on the oxygen thereby causing it to behave as a trivalent atom. As a consequence the oxygen atom attempts to form a bond with atoms that approach within bond length distance. Thus it may tend to form an additional bond with the carbon atom to which it is already attached and as a consequence the other three bonds of that carbon are weakened.

The various products formed during the radiolysis of liquid ethanol, and their G values given in parenthesis, are (85): hydrogen (3.46), acetaldehyde (1.71), vicinal glycols (1.05), water (0.81), methane (0.43), formaldehyde (0.30), ethane (0.17), ethylene (0.17) and carbonmonoxide (0.11).

To find the possible modes of hydrogen formation, Burr (88) studied the Co^{60} γ-radiolysis of a series of five deuterated ethanols. From the rates of hydrogen production and mass-spectral studies (89), Burr proposed a mechanism for the radiolytic decomposition of ethanol.

$$CH_3CH_2OH \rightsquigarrow CH_3CH_2OH^* \qquad \text{--(1)}$$

$$CH_3CH_2OH \longrightarrow CH_3CHOH + H \quad (100\%) \qquad \text{--(2)}$$

$$H + CH_3CH_2OH \longrightarrow H_2 + CH_3CH_2O \quad (80\text{-}90\%) \quad --(3)$$

$$H + CH_3CH_2OH \longrightarrow H_2 + CH_2CH_2OH \quad (10\text{-}20\%) \quad --(4)$$

$$2\ CH_3CHOH \longrightarrow (CH_3CHOH)_2 \quad --(5)$$

$$2\ CH_3CHOH \longrightarrow CH_3CHO + CH_3CH_2OH \quad --(6)$$

$$2\ CH_3CH_2O \longrightarrow CH_3CHO + CH_3CH_2OH \quad --(7)$$

It appeared that hydrogen production proceeded via a radical process wherein the hydrogen atoms originated almost exclusively from the $-CH_2$ group. From the measurements of the deuterium content of the radiolytic hydrogen, it was concluded that the ensuing abstraction reaction occurred principally on -OH hydrogen by reaction (3), with a small amount occurring at the CH_3 group by process (4). In the above mechanism, no mention was made of the fate of (CH_2CH_2OH). It also left water, methane and formaldehyde unaccounted for.

Burr gives as evidence in support of reactions (5), (6) and (7) the fact that since the aldehyde can be formed from both radicals and the glycol can only be formed from only one, there should be twice as much aldehyde as glycol; the G values for aldehydes and glycols in Mc Donell and Newton's work were 2.2 and 1.05, respectively. This assumes that the rates of reactions (5) and (6) are equal

but no reason was given for this assumption.

The primary process demonstrated above is the rate determining cleavage of a C-H bond followed by a rapid hydrogen abstraction. The values of k_H/k_D (ratio of rates of H and D formation), which have been observed for a number of rate determining C-H bond cleavages which occur near room temperature, range from 6 - 10 (90). This ratio decreased with increasing reaction temperature to a minimum value of 1.4 (90). Burr evaluated this ratio from his experimental data and found the ratio to be 1.3. This suggests that the rate determining process in ethanol radiolysis is one of high equivalent temperature. In other words, the primary disengagement of hydrogen atoms occurs from a molecule of high energy content (an excited or ionised species). This is one of the first experimental confirmations of the postulated excited species in the radiolysis of organic compounds.

(D) Dosimetry

The amount of change brought about in an irradiated system is often proportional to the amount of energy actually absorbed. The amount of energy absorbed, in ergs per gram of the irradiated material, is called the physical dose. The measurement of this dose is the subject that

constitutes dosimetry. Before going into the various methods of measurement, it would be proper to understand the units used in dosimetric measurements.

Most of the earlier measurements were expressed in terms of the roentgen. The definition of the roentgen reads: "One roentgen is the quantity of X - or γ -radiation such that the associated corpuscular emission per 0.001293 grams of air produces, in air, ions carrying 1 e.s.u. of quantity of electricity of either sign" (91). Roentgens per minute is a unit of beam intensity.

Another important unit is the rad. The rad is a unit of dose and corresponds to the absorption of 100 ergs per gram. The measurement of dose in terms of rads has an advantage over that measured in roentgens. Since the roentgen is a unit of beam intensity and is related to the ionisation of air, to convert roentgens into energy absorption in a specimen, the amount of energy required to produce an ion pair (W) must be known. As experimental determinations of W have varied, so has the figure for energy absorption. Where the basic measurements are carried out in terms of the rad, this factor no longer intervenes (45).

A number of physical methods involving the use of ionisation chambers (93), calorimeters (94) and other

instruments (95,96), can be used to measure the energy absorbed. In this chapter, however, only chemical methods of measuring dose are described.

Solid, liquid and gas phase chemical systems have been employed in dosimetry.

Among the gel and solid dosimeters, resazurin in agar (97) and chloral hydrate-agar gel (98) are well known and are useful for depth dose measurements. The chloral hydrate-agar gel dosimeter requires a minimum dose of 2000 rads for reasonable accuracy. These systems change colour with increasing energy absorption.

Among the gas phase dosimeters, the decomposition of nitrous oxide and the condensation of acetylene are in use. Harteck and Dondes (99) suggested a dosimeter based on the decomposition of nitrous oxide into oxygen, nitrogen and nitrogen di oxide. The doses can be measured either from the nitrogen plus oxygen evolved or from the nitrogen di - oxide. The nitrous oxide dosimeter can be used in the range 5×10^4 to about 10^8 rads. The condensation of acetylene to benzene (G (benzene) = 5.1) was suggested as a dosimeter by Dorfman and Shipko (100). This acetylene system appears to be preferred by workers in the vapour phase and is independent of the initial acetylene pressure and radiation intensity.

Acidic solutions of ferrous sulphate, called the

Fricke dosimeter (101,102) and of ceric sulphate (103,104, 105) are the familiar ones in the class of liquid dosimeters. The ceric sulphate system, though similar to the ferrous sulphate system in its concentration and energy independence, is still not very popular on account of its extreme sensitivity to impurities. The Fricke dosimeter is the most widely used and is considered most reliable.

The Fricke dosimeter solution is prepared by dissolving ferrous ammonium sulphate (1 mM) and sodium chloride (1 mM) in 0.8 N sulphuric acid. The reagents used must be analytical grade and the water must be doubly distilled. The ferrous ions get oxidised to ferric ions under the influence of the ionising radiation. The ferric ion concentration is usually estimated spectrophotometrically by measurement at 304 mμ. There is a spectrophotometric temperature coefficient of about 0.8 percent per centigrade degree between 20°C and 30°C (106,107). The useful range of this dosimeter is from 4 to 40 K.rads; but it can be extended to 200 K.rads by saturating the solution with oxygen and increasing the ferrous sulphate concentration (92). Best results are obtained when concentrations of ferrous ions are kept between 1 mM and 0.1 mM (92,108).

The Fricke dosimeter can be modified for use both at low doses (0 - 100 rads) and high doses (up to 10^6 rads).

The low dose measurements involve the use of Fe^{59} as a tracer (109). The applicability of the Fricke dosimeter for high doses was developed by Hart and Walsh (110) by using 1 mM ferrous ion, 10 mM copper sulphate and 0.01 N sulphuric acid.

As has already been mentioned (Sect. A, Page 7), alpha particles and electrons differ from one another in the density of ionisations and excitations they produce along their paths. This difference is due to the varying amounts of energy loss per unit path length sustained by the ionising particles. This energy loss is quantitatively described in terms of an average energy loss per unit path length (linear energy transfer, LET). Heavy particles such as alphas sustain greater LET due to their low velocity and as a consequence produce tracks of continuous ionisation and excitation. Faster charged particles such as electrons suffer a smaller LET and produce tracks of ionisation and excitation of lower density.

This LET effect is very well illustrated in the different yields of Fe when ferrous sulphate is irradiated by alpha particles and electrons.

The general reactions postulated to explain the formation of Fe are as follows:

$$H_2O \longrightarrow H + OH$$

$$\longrightarrow H_2O_2 + H_2$$

$$OH + Fe^{++} \longrightarrow OH^- + Fe^{+++}$$

$$H + O_2 \longrightarrow HO_2$$

$$HO_2 + Fe^{++} \longrightarrow Fe^{+++} + HO_2^-$$

$$HO_2^- + H^+ \longrightarrow H_2O_2$$

$$H_2O_2 + Fe^{++} \longrightarrow OH + OH^- + Fe^{+++}$$

$$OH + Fe^{++} \longrightarrow OH^- + Fe^{+++}$$

From the above equations, it is evident that each hydrogen atom produces three ferric ions. In the case of electrons, hydrogen atoms are produced in sparsely distributed hot spots and hence will be available for the above reactions. In the case of alpha particles, due to the presence of continuous columns of ionisation and excitation, there will be greater chance for hydrogen atoms to recombine to form H_2 and thus not be available for the above reactions. This decreases the ferric ion yield in the case of alpha irradiation.

Thus in the literature, values of G (Fe^{+++}) for Po^{210} alpha particles ranging from 4.7 to 6.2 (111 - 118)

have been reported. These values are far lower than the generally accepted value for G (Fe^{+++}) = 15.5 (92) in the field of X-, γ- and β-ray dosimetry. In the present thesis, an average value of G (Fe^{+++}) = 5.5, has been adopted to calculate the energy output of the Po^{210} source.

(E) Scope of the Present Work

Both C-C and C-H bonds can be broken when hydrocarbons are irradiated and the highly reactive fragments formed are capable of a variety of reactions, including reaction with each other. As both C-C and C-H bonds are broken, the products formed are hydrogen and hydrocarbons of both higher and lower molecular weights than the original. Primary ionisations and excitations occur in all the physical states of a system but the reactions of the ions and excited molecules might be dependent on the state. Different product yields have been observed in the different phases. In the liquid phase, the rate of formation of hydrogen and of lower hydrocarbons appears to be less than that in the vapour, possibly owing to collisional deactivation or to a greater extent of radical recombination within the liquid cages. To investigate the differences in the radiolyses of liquids and vapours, in this laboratory the radiolyses of cyclohexane, methyl cyclohexane and ethanol and of the mixtures

of each with benzene and cyclohexene are being investigated in both liquid and vapour phases. This thesis is confined to the vapour phase radiolyses of the above mentioned compounds and their binary solutions, using Po^{210} alpha particles.

II EXPERIMENTAL

(A) Apparatus

The apparatus used in these investigations consists of three manifolds, inter-linked with one another. They are:

(1) the main manifold where the gaseous reaction products were measured.

(2) the auxiliary manifold which served the two fold purpose of discarding waste gases after being measured in the McLeod - Toepler gauge and transferring the pure samples from the reservoir into the main manifold for irradiation purposes.

(3) the calibration manifold used for determining the calibration constants of gases which were expected to be products from the irradiations of various hydrocarbons and the alcohol.

A brief description of each of these manifolds follows:

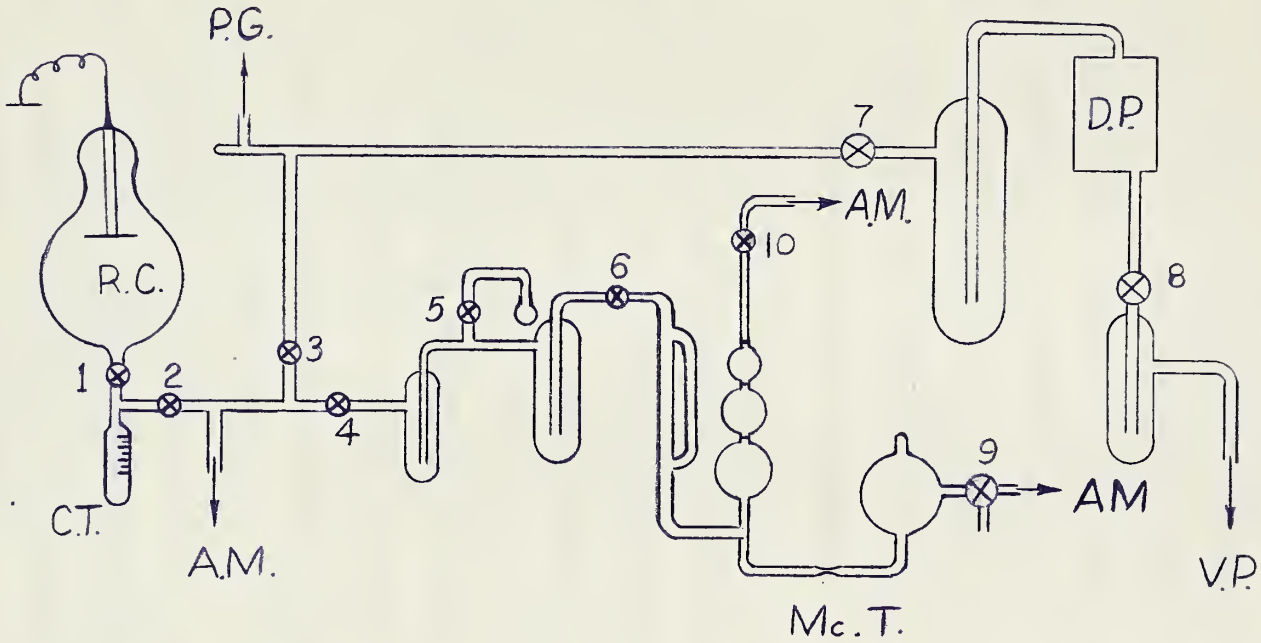
(a) Main manifold

Figure 1 is a diagram of the main manifold. The reaction chamber, where the irradiations were carried out, consisted of a one litre bulb fitted with an outer B19 (24/40 in the later experimental work) ground glass joint at one

Figure 1

R.C.	Reaction chamber
C.T.	Calibrated tube
A.M.	Auxiliary manifold
P.G.	Pirani gauge
Mc.T.	McLeod gauge-Toepler pump combination
D.P.	Mercury diffusion pump
V.P.	Mechanical vacuum pump
1 - 10	High vacuum stopcocks

Figure 1


P.G.
R.C.
1
2
3
4
5
6
7
A.M.
10
D.P.
8
C.T.
A.M.
9
AM
V.P.
Mc.T.

end and a high vacuum stopcock at the other end.

Figure 2a represents the Po^{210} probe. An inner B19 (or 24/40) joint was made into a test tube and a glass tube with a tungsten seal was passed through the B19 (or 24/40) and fused in a condenser seal. The Po^{210} alpha source was cemented to this glass tube by a mixture of araldite 502 and catalyst araldite 951 in the proportions 10:1. A copper wire soldered to the stem of the polonium probe was attached to the tungsten wire in the inner glass tube and this tungsten wire was grounded to insure that a negative charge did not build up on the polonium source. Such a build up of charge might have increased the tendency for polymer to form on the probe, thereby ruining the source.

The B19 (or 24/40) joint with the Po^{210} source was fitted into the outer B19 (or 24/40) of the litre bulb, using silicone grease. The junction was covered with an improved type of Dekhotinsky cement. A furnace was constructed around the reaction vessel using nichrome wire (2 ohms per foot resistance) and asbestos. This enabled one to heat the whole vessel keeping the reactants in the vapour phase during irradiation. A copper-constantan thermocouple, buried in the asbestos against the wall of the reaction chamber was used in conjunction with a potentiometer (Leeds and Northrup) to measure the temperature of the litre bulb.

Figure 2a

Figure 2b

Figure 2c

Figure 2a

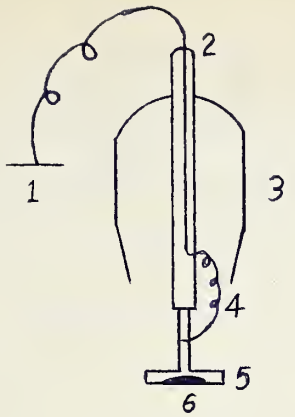
1. Ground
2. Tungsten wire
3. B19 inner joint
4. Copper wire
5. Polonium source
6. Active surface

Figure 2b

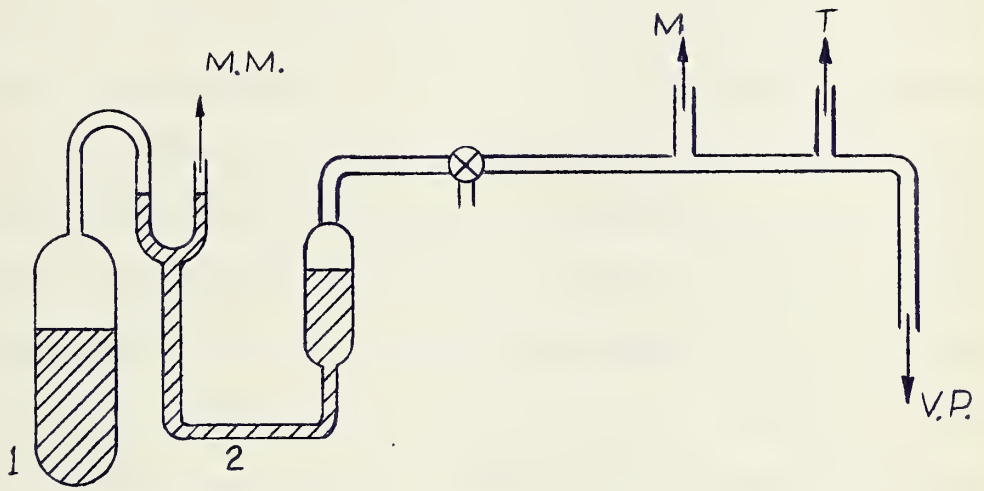
M.M. Main manifold
M. Mc Leod gauge
T. Toepler pump
V.P. Vacuum pump
1. Reservoir containing the liquid for irradiation
2. Mercury cut-off

Figure 2c

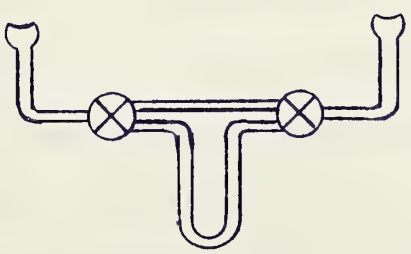
Gas sampler



a



b



c

The bulb was attached to a calibrated tube through stopcock 1. Two small traps were connected to the calibrated tube through stopcocks 2 and 4. These two small traps which served for trapping the liquids before the gases were measured, were connected to a Toepler pump - Mc Leod gauge combination through stopcock 6. A small test-tube with a 12/30 joint was attached through stopcock 5 to the main manifold. This test-tube facilitated the introduction of fresh samples into the main manifold and taking out the irradiated ones from the manifold for analysis. In the construction of this section of the manifold, the apparatus was made as compact as possible to keep the volume to a minimum. Stopcock 3 connected this section to a long glass tube (25 mm O.D.) into which a pirani gauge (Consolidated Vacuum Co. model 2201-03) was sealed. This long tube was connected to a Welsch duo-seal vacuum pump through a succession of stopcock 7, a cold trap, a mercury diffusion pump, stopcock 8 and a cold trap.

(b) Auxiliary manifold

Figure 2b represents the auxiliary manifold. A reservoir (to store the vacuum distilled liquids to be irradiated) was connected to the main manifold via a mercury cut-off. The other end of the mercury cut-off was connected to a Welsch duo-seal vacuum pump through a three way stopcock.

From the exit end of the Mc Leod gauge, the gaseous products were removed for gas chromatographic analysis on a Burrell Kromo-Tog K2 in a specially designed cell as shown in Figure 2c. This cell was connected to the auxiliary line through a 12/2 hemispherical joint.

(c) Gas calibration manifold

Three one-litre bulbs provided with stopcocks were joined to a 10 mm glass tubing. This glass tubing in turn was connected to the main manifold by a three way stopcock. As a continuation of this glass tubing and beyond the three way stopcock, a small cold trap and a mercury gas bubbler were connected by 12/2 hemispherical joints. This manifold enabled one to put the required gases into the bulbs and transfer them to the specially designed gas sampler for analysis. A mercury manometer situated just before the three way stopcock facilitated the measurement of the pressures of gases. Aliquots of each gas at different pressures were thus taken out and analysed.

(B) Materials

All the chemicals that were used in these investigations except ethanol were employed without further purification. The percent impurities in each case were determined by gas chromatography. Eastman Kodak spectrograde chemicals

were always used unless otherwise stated.

(a) Cyclohexane

In the various samples of cyclohexane used, the impurities did not exceed 1 mole percent. The spectrograde cyclohexane was purified by vacuum distillation, retaining the middle 70 - 80 percent. Two sets of runs, one with the purified and another with the unpurified cyclohexane, did not show any difference in the gaseous product yields. Thereafter the cyclohexane was used without purification. The sample of cyclohexane used in the inhibition studies showed a maximum impurity of about 0.2 mole percent.

(b) Benzene

The benzene contained 0.22 mole percent impurities.

(c) Cyclohexene

Cyclohexene from Matheson, Coleman and Bell had impurities totalling up to about 0.1 mole percent.

(d) Propylene

Propylene, used in the inhibition studies, was Phillips Research grade containing about 0.1 mole percent impurities.

(e) Methyl Cyclohexane

Methyl cyclohexane had impurities up to 0.6 mole percent.

(f) Ethanol

The ethanol was from Reliance Chemical Ltd., containing about 0.11 mole percent water. Three and a half grams of sodium were dissolved in 500 cc of ethanol and 14 grams of diethyl phthalate was added to this solution (119). This solution was refluxed for two hours and was distilled in a system protected from moist air by passing dry hydrogen through it. After the purification, the ethanol contained only 0.005 mole percent water.

(g) The Alpha source

Several one-hundred millicurie Po^{210} sources (half life of Po^{210} = 138.4 days) were obtained from Atomic Energy of Canada Limited. Po ^{210} alpha particles have an energy of 5.309 ± 0.003 Mev (120). The active surface of this source was protected by a thin mica film which reduced the average energy by about 30 percent. Each source was calibrated with the Fricke dosimeter before it was installed in the reaction chamber.

(C) Techniques

(a) Standardisation of the Po^{210} sources

All the glass-ware that was used in these calibrations was thoroughly cleaned by keeping it immersed in hot sulpho-nitric acid for about twenty minutes, washed several

times with tap water, followed by washing twice with doubly distilled water (distilled over alkaline potassium permanganate and redistilled) and dried in an oven. Two sets of ferrous ammonium sulphate solutions were prepared in 0.8 N sulphuric acid: (1) 1 mM sodium chloride and 1 mM ferrous ammonium sulphate and (2) 1 mM sodium chloride and 3 mM ferrous ammonium sulphate. Three mls of each of these samples were pipetted into clean 5 ml beakers and the Po^{210} source was positioned about 2 - 3 mm above the surface of this solution by a screw and prong arrangement. The solutions were thus irradiated for periods of 5, 10, 15 and 20 minutes and the extent of oxidation was measured with a Cary spectrophotometer (model No. 14 M). The molar extinction coefficient used in these calculations is 2225 at 25°C. The optical density increase per minute in each case (both in 1 mM and 3 mM solutions) was in excellent agreement with each other. Special care was taken to exclude impurities, including dust from the atmosphere, which produce very erratic results. Due precautions were taken in handling this radioactive source. The energy output of the source was computed by assuming $G\ (Fe^{+++}) = 5.5$.

(b) Preparing the samples for irradiation

Two mls of the vacuum distilled cyclohexane stored in the reservoir were distilled into the calibrated tube

The cyclohexane sample was degassed in the calibrated tube by the usual thawing - freezing - pumping technique. This sample was volatilised into the heated reaction chamber by submerging the calibrated tube in boiling water. When all the cyclohexane was volatilised into the reaction chamber, the stopcock 1 was closed and the sample was irradiated.

Alternatively, the sample of cyclohexane was introduced into the reaction chamber by a pipetting technique. Two mls of cyclohexane were pipetted into the small reservoir near stopcock 5. This sample was cooled to -196^{o}C and degassed. It was then distilled into one of the small traps, cooled in liquid nitrogen, pumping on it all the while. After closing stopcock 5, the sample was distilled from the trap into the calibrated tube where it was degassed again. The sample was then volatilised into the reaction chamber as before.

The product yields were the same within experimental error in both cases. Hence the easier pipetting method was always employed in the course of these studies, except for some of the ethanol experiments. The dose function studies in ethanol irradiations were performed by sampling the ethanol by the first method. For all inhibition studies, the pipetting technique was always followed for sampling.

(c) Analytical techniques

The gases generated during the irradiations of hydrocarbons were hydrogen, methane, C_2, C_3 and C_4 hydrocarbons. Ethanol irradiation gave rise to hydrogen, methane, carbon monoxide and C_2 hydrocarbons.

The irradiated sample was condensed from the reaction chamber into the calibrated tube, cooled to - 196°C. The non-condensable gases were hydrogen, carbon monoxide and methane. These gases were distilled through two liquid nitrogen traps and were measured as a total in the Mc Leod gauge. They were then taken out in the gas sampler and analysed. A one-metre charcoal column, with helium carrier flow rate $\simeq$ 56 ml per minute and column temperature of about 120°C, was used for the analysis. Hydrogen, carbon monoxide and methane appeared as well resolved peaks. These peaks were quantitatively estimated by doing standard calibration experiments, to be described later. All the hydrogen, carbon monoxide and methane were taken out of the liquid condensate by melting and freezing twice during Mc Leod - Toepler measurements.

Another fraction of gases, non-condensable at -112°C, was separated from the irradiated liquid sample by distilling through traps cooled by an ethyl alcohol-liquid nitrogen slush bath. This fraction essentially consisted of

ethane, ethylene, propane, acetylene, propylene, some methane and C_4 hydrocarbons. This - 112°C fraction, after being measured in the Mc Leod - Toepler gauge, was collected in the gas sampler and analysed using a 2.5 metre silica - gel column. The carrier gas, helium, had an initial flow rate of 115 ml per minute and the temperature of the column was varied from room temperature to a maximum of 250°C. The quantitative estimation of each of these products was achieved by doing calibration experiments.

The irradiated sample was finally removed from the manifold by distilling it into the small test tube near stop-cock 5. The chromatographic columns used for the analyses of various liquid products together with the conditions employed for the analyses are summarised in Table I.

To program the temperature of the columns during analysis, the Burrell variac was set in all cases except apiezon L column to the voltage indicated in Table I as soon as the air peak emerged. The 1 metre apiezon column was heated by setting the Burrell variac at 20 volts as soon as the sample was injected (causing a variation from room temperature to about 110°C) and altering it to 40 volts after the cyclohexane peak emerged (110°C to about 240°C).

Blank chromatograms of unirradiated compounds were run during the analyses of liquid products in the case of

TABLE 1

The Columns and Conditions used for the Analyses of Liquid Products

	Liq. Products analysed	Column used	Carrier Gas & its flow rate (ml/min)	Burrell Variac setting for heating the Columns	Temp. of the column
1.	Cyclohexene Various C_{12} hydrocarbons	2.5 m Silica-gel	Hydrogen, 54	100 Volts	room temp. to about 250°C
2.	Total C_{12} hydrocarbons	1 m Apiezon L	Hydrogen, 51	20 V initially & 40 V later	room temp. to about 240°C
3.	Cyclohexane Benzene	1 m Silver Nitrate-Glycerol	Helium, 62	4.5 Volts	51°C
4.	Water	2.5 m Carbowax	Hydrogen, 113	43 Volts	room temp. to about 130°C
5.	n-Propanol n-Butanol Various Glycols	2.5 m di-decyl phthalate	Hydrogen, 150	56 Volts	room temp. to about 175°C
6.	Total Glycols	1 m Ucon	Hydrogen, 55	25 Volts	room temp. to about 170°C

all the columns. One hundred microlitre liquid samples were injected each time.

The thermocouple - pyrometer was inaccurate and so was calibrated. With the aid of a pyrometer calibration curve, the correct temperatures of these columns were determined and are the ones given in Table I.

In the case of ethanol irradiation, formaldehyde was estimated by chromotropic acid method (121) and acetaldehyde was determined by polarography (122).

(d) Calibration factors

(1) Hydrogen, Methane and Carbon monoxide

The calibration manifold and the bulbs were filled with the particular gas. Various amounts of the gas were taken from the bulbs into the gas sampler (calibrated volume = 5.8 ml), noting the pressure of the gas in each case with the aid of the manometer. Chromatograms of these were run on the 1 m charcoal column, using the conditions as previously stated. Since the peaks were too narrow to permit precise area measurements, plots were made with peak height as the ordinate and the pressure of these samples as the abscissa. These peak height - pressure plots were used in determining the amounts of any of these gases in any individual experiment from the respective chromatogram.

(2) Gases volatile at - 112°C

Each of these products was standardised by the same technique as above. The area of the peak per mm pressure of gas in the gas sampler was computed for each product. This calibration factor appeared to be independent of the pressure for each of the gases. The calibration factors were expressed in sq. mm area per mm of gas in the gas sampler (5.8 ml) at room temperature.

(3) Liquids

Calibration factors for various liquid products, using the appropriate column and conditions described in Table I, were determined. For this purpose, standard solutions of the appropriate compounds in cyclohexane or ethanol were prepared by weighing. These solutions were analysed using the Kromo - Tog and the ratio of the peak area of the compound to that of cyclohexane or ethanol was calculated. The ratio of the peak areas was divided by the mole ratio to determine the calibration factors. These calibration factors were used for quantitative estimation of the liquid products in the irradiated sample.

III RESULTS

(A) Calibrations

(a) The - 196°C fraction

The gases that were not condensable at - 196°C were hydrogen, methane and carbon monoxide. The gas chromatographic calibrations of these gases were performed using a 1 m charcoal column, employing the conditions described in Chapter II. Table II (a) gives the pressure (P, in cms of mercury) versus peak height (P.H., in cms) data for hydrogen and methane. Since the ethanol irradiations were done about two years later than cyclohexane irradiations, the relative sensitivities of hydrogen, methane and carbon monoxide were determined and are tabulated in Table II (b). The new hydrogen and methane calibrations had changed by a factor of 4.6 $\pm$ 0.2. Since the relative sensitivities of the two gases remained the same, either set of curves could be used to calculate the relative amounts of the gases in the - 196°C fractions.

The old calibrations for hydrogen and methane were used for calculations of yields in irradiation of hydrocarbons and the new calibration factors for hydrogen, carbon monoxide and methane were used to calculate the yields in ethanol radiolysis.

TABLE II (a)

Pressure - Peak Height Data for Hydrogen and Methane

Irradiations of hydrocarbons

	Hydrogen		Methane	
	P (cms)	P.H.(cms)	P (cms)	P.H.(cms)
1.	0.4	0.35	0.9	9.7
2.	0.7	0.50	1.6	18.1
3.	1.9	1.15	2.7	31.0
4.	4.1	1.75	7.6	81.5
5.	6.6	0.20	12.4	120.8
6.	8.6	0.50	21.8	184.0
7.	10.5	1.80	30.8	232.0
8.	11.9	2.65	34.7	244.0
9.	15.1	5.00	43.8	290.0
10.	21.0	12.20		
11.	33.6	28.60		
12.	42.1	40.50		
13.	43.6	49.75		
14.	56.9	61.50		

TABLE II (b)

Pressure - Peak Height Data for Hydrogen, Carbon monoxide and Methane

Irradiations of ethanol

	Hydrogen		Carbon monoxide		Methane	
	P (cms)	P.H.(cms)	P (cms)	P.H.(cms)	P (cms)	P.H.(cms)
1.	0.6	0.1	0.6	69.0	1.6	79.5
2.	2.0	0.54	1.1	108.5	2.2	114.0
3.	3.4	3.0	1.7	187.0	2.9	136.0
4.	5.8	21.0	2.4	218.0	6.0	228.0
5.	7.1	33.0	5.3	420.0	7.2	270.0
6.	10.4	54.0				

Figures 3 and 4 are the graphical representations of these data.

The broken curve B, in the positive region of Figure 3 was obtained by multiplying the A curve in the positive region by the ratio of B to A (1 : 4.6) in the negative region.

(b) The - 112°C fraction

The gases that were volatile at - 112°C emerged on a silica-gel column in the following order: methane, ethane, ethylene, propane, acetylene, propylene, butane and butylene. The calibration factors for each of these gases were calculated and are tabulated in Table III. The calibration factor for any gas is defined as the area of the chromatographic peak in sq. mm per mm pressure of the gas at room temperature in the 5.8 ml of the gas sampler.

(c) Liquid products

The calibration factors for the various products remaining in the cyclohexane liquid after distillation into the traps at - 112°C were determined on 2.5 m silica-gel and 1 m apiezon L columns under the conditions stated in Table I. These factors are presented in Table IV. The calibration factors for the various liquid products in ethanol liquid were determined on 2.5 m carbowax 1500, 2.5 m di-decyl phthalate and 1 m ucon columns. These values are

Figure 3

Figure 3

Hydrogen Calibration Curve

P.H. Peak height in cms.

P. Pressure in cms.

A. Old calibrations.

B. New calibrations.

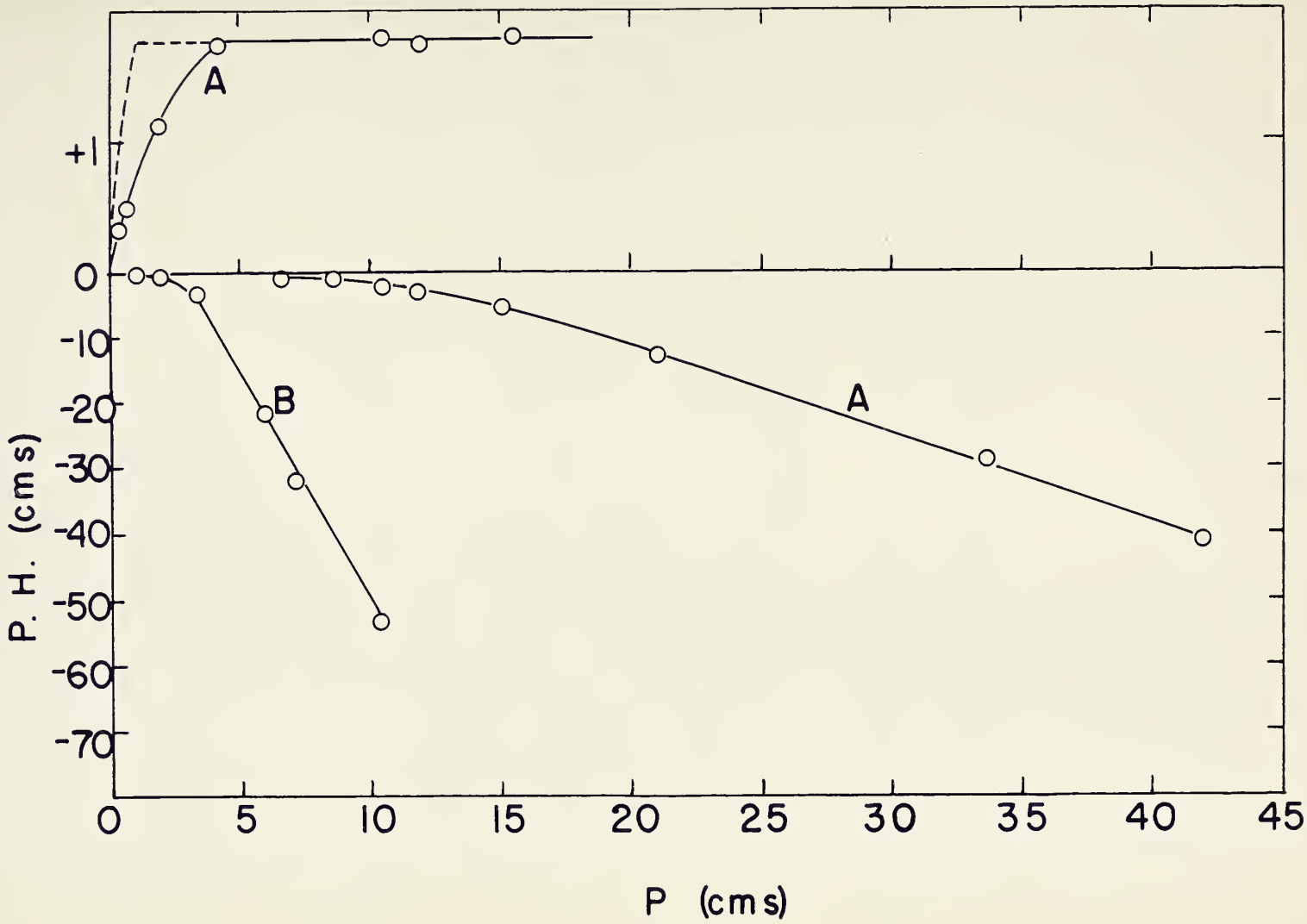

A
+1
0
-10
-20
-30
-40
-50
-60
-70
B
A
P. H. (cms)
0
5
10
15
20
25
30
35
40
45
P (cms)

Figure 4

Figure 4

Methane and Carbon monoxide Calibrations

P.H. Peak height in cms.

P. Pressure in cms.

A. Old methane calibrations.

B. New methane calibrations.

C. Carbon monoxide calibtations.

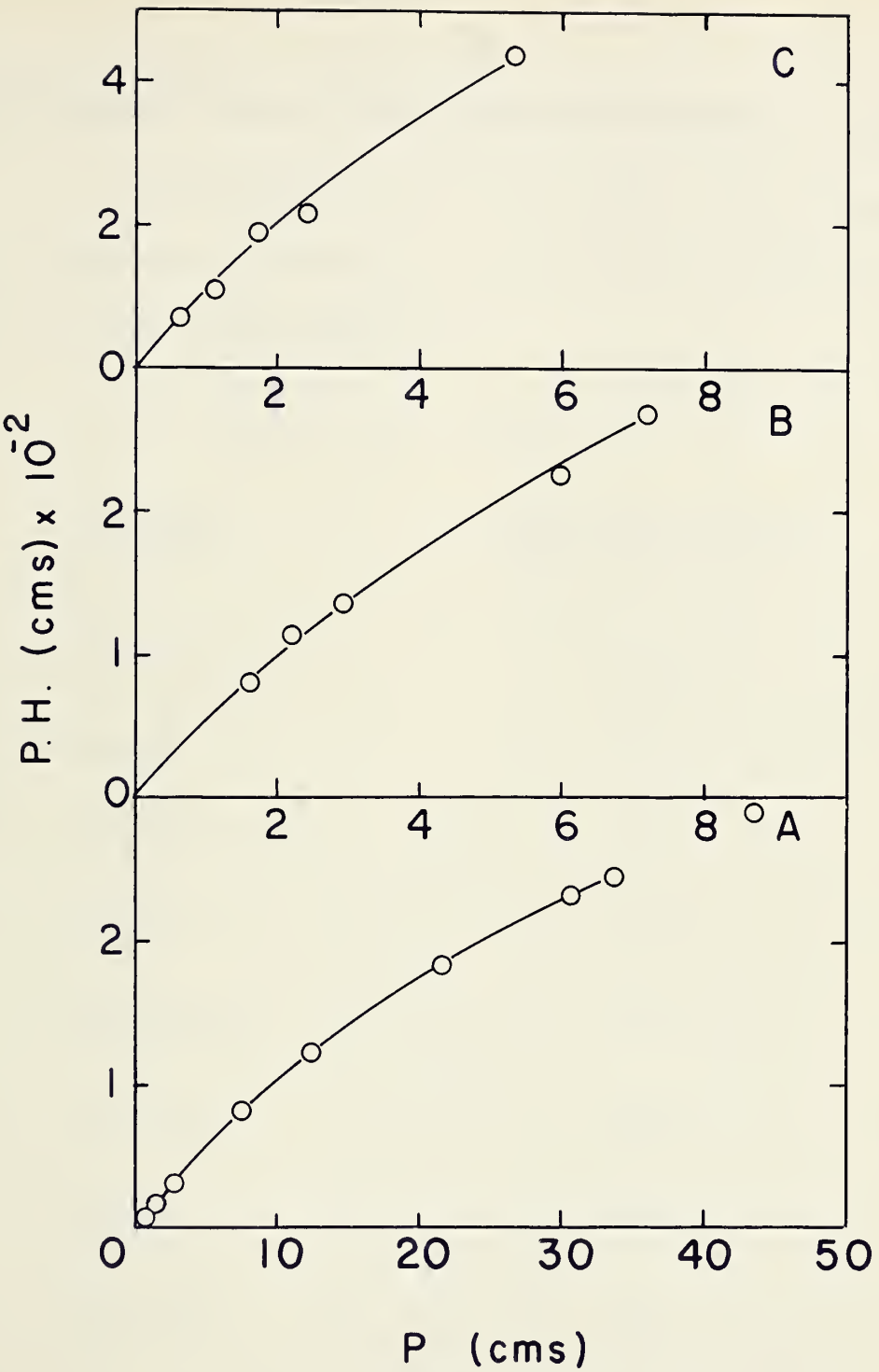

C
B
A
P.H. (cms) x 10⁻²
P (cms)
0
2
4
6
8
10
20
30
40
50
1

TABLE III

Calibration Factors of Gases Non-condensable at - 112°C

Calibration factor is the area of the peak (sq. mm) per mm pressure of gas at room temperature in 5.8 ml of gas sampler.

Silica - gel column

	Compound	Calibration factor
1.	Methane	15.4
2.	Ethane	25.2
3.	Ethylene	23.3
4.	Propane	41.0
5.	Acetylene	21.5
6.	Propylene	36.0
7.	Butane	67.0
8.	Butylene	57.0

TABLE IV

Calibration Factors for the Various Hydrocarbons Obtained in Cyclohexane Radiolysis

Calibration factor is obtained by dividing the area ratio (from the chromatogram) by mole ratio.

2.5 m Silica - gel column

	Compound	Calibration factor
1.	C_3 hydrocarbon	0.8
2.	C_4, C_5 hydrocarbons	0.9
3.	C_8, C_9, C_{10} hydrocarbons	1.9
4.	C_{11}, C_{12} hydrocarbons	2.0

1 m Apiezon L column

	Compound	Calibration factor
1.	C_3 hydrocarbon	0.8
2.	C_4 hydrocarbon	0.9
3.	C_8, C_9 hydrocarbons	1.57
4.	C_{10} hydrocarbon	1.7
5.	C_{11}, C_{12} hydrocarbons	1.8

given in Table V. The calibration factor for any liquid product is the ratio obtained by dividing the area ratio by mole ratio in a standard solution of the product in the original compound (cyclohexane or ethanol).

(B) Irradiations

(a) Calibration curves

In the preliminary experiments, two mls of cyclohexane were irradiated for various lengths of time and the gaseous products, non-condensable at - 196°C, were measured in the Mc Leod - Toepler gauge. These results indicated that the Po^{210} source became weak in long irradiations due to polymer formation on the source. Consequently all the inhibition experiments of cyclohexane, methyl cyclohexane and ethanol were performed for two hours only.

The dose function experiments with pure cyclohexane, methyl cyclohexane and ethanol were performed for various lengths of time. In order to determine the dose and the yields in these experiments, two hour cyclohexane runs were done periodically. From these cyclohexane runs, a calibration curve was constructed. One such calibration curve, employed in the cyclohexane dose function and inhibition runs, is shown in Figure 5. Since the calibration curve was linear, the energy output of the source for any given

TABLE V

Calibration Factors of the Various Liquid Products

Obtained in Ethanol Radiolysis

Calibration factor is obtained by dividing the area ratio (from the chromatogram) by mole ratio.

	Compound	Calibration factor		
		2.5 m Carbowax 1500 column	2.5 m Didecyl phthalate column	1 m Ucon column
1.	Water	0.6	-	-
2.	Propanol	-	0.8	-
3.	Butanol	-	1.1	-
4.	1,2 Propane diol	-	1.2	-
5.	2,3 Butane diol	-	1.2	-
6.	1,4 Butane diol	-	1.3	-
7.	Total glycol	-	-	1.0

Figure 5

Figure 5

Calibration Curves used to Estimate the Correct Dose and Yield

Irradiation temperature = 108°C

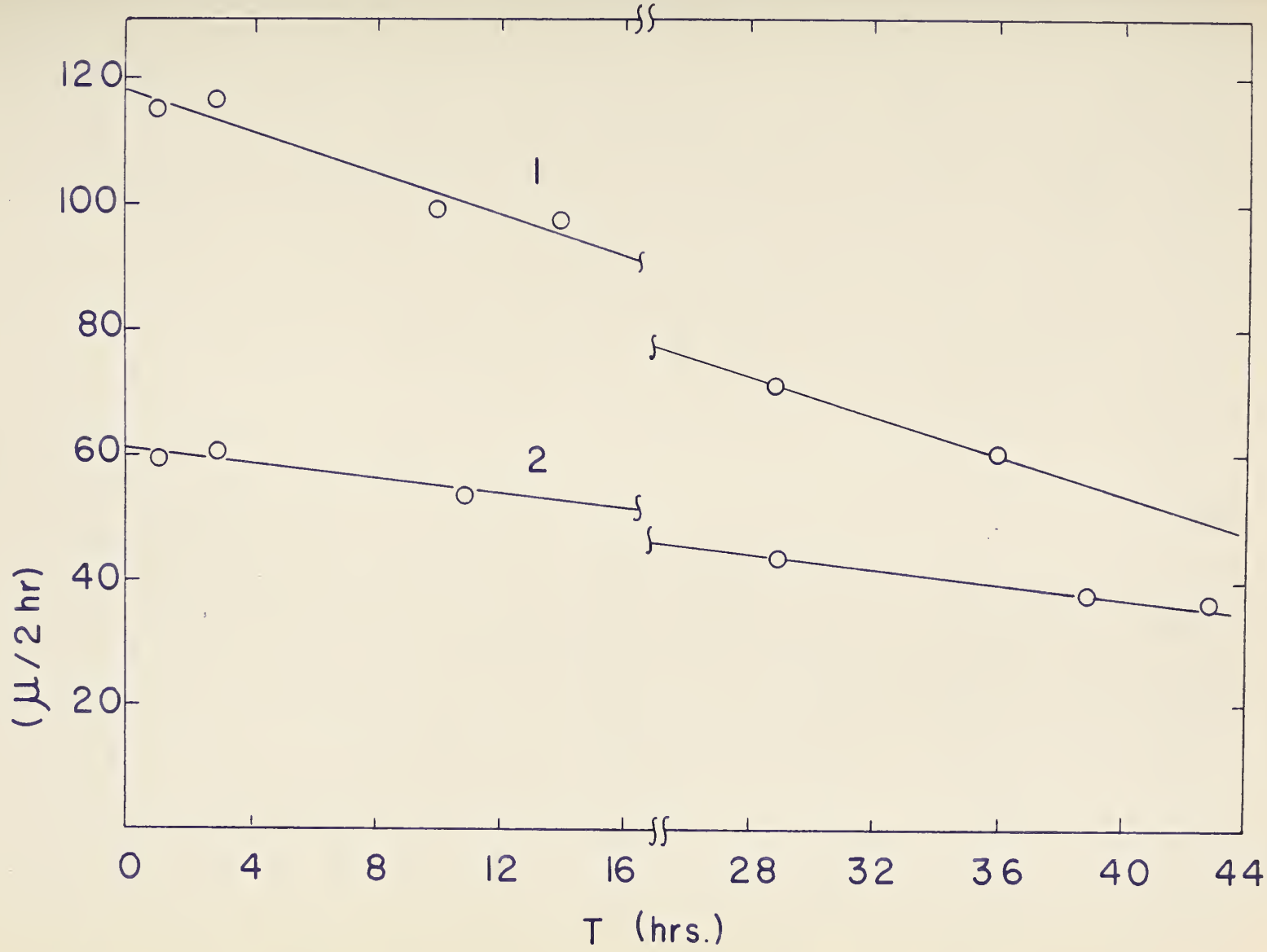
μ = microns of gas at S.T.P.

1. Calibration curve for cyclohexane dose function runs

   cyclohexane 2 hour runs

2. Calibration curve for cyclohexane inhibition runs

   cyclohexane 2 hour runs


120
100
80
60
40
20
(μ/2 hr)
1
2
0
4
8
12
16
28
32
36
40
44
T (hrs.)

experiment was taken from the curve at the time corresponding to the mid point of the run. Such a calibration curve included the radioactive decay correction for the Po^{210}.

(b) Blank runs

Blank runs were done in order to estimate the amount of air left dissolved in the liquids after degassing procedures had been followed.

Blank runs of cyclohexane, methyl cyclohexane, ethanol, benzene, cyclohexene and propylene were performed by volatilising them into the chamber, closing stopcock 1, pumping the residual vapours from the calibrated tube, then opening stopcock 1 and condensing the material into the calibrated tube. This was done as rapidly as possible to minimise the radiolysis of the substance and required about one minute. The substance was then analysed by the procedure used for the regular samples. The amounts of gases volatile at - 196°C were 6 ± 2 percent of the amounts obtained from the respective compound in a two hour run. The only exception was ethanol, in which the blank was only 2 percent of the corresponding two hour run. The percent values obtained for the - 112°C distillation were: cyclohexene 0, benzene 4, ethanol 5, methyl cyclohexane 7, and cyclohexane 12. No -112°C

blanks could be obtained for propylene because it was volatile at this temperature.

The blank run values were substracted from the yields in every dose function experiment and the net yields were used to calculate the G values. However, blank run values were not substracted in any inhibition experiments. This was due to the fact that the blanks were nearly constant at about 6 percent of the two hour yield. Hence the overall kinetics will not be much affected.

(c) Cyclohexane radiolysis

(1) Radiolysis of cyclohexane as a function of volume

In an attempt to determine the pressure of cyclohexane which would absorb all the energy of the alpha particles emitted by the source, different amounts of cyclohexane were irradiated for a period of four hours each. The total yields of gas, non-condensable at - 196°C, were measured and are presented in Table VI and Figure 6. The pressure of cyclohexane vapour is also given at the temperature of the reaction chamber, about 108°C.

From Figure 6, it is evident that the yield of gas increases with increasing amount of cyclohexane and reaches a constant value at about two mls of cyclohexane. Thus it may be assumed that all the energy was absorbed from the

TABLE VI

Yield of Gas Volatile at - 196°C as a Function of Volume of Liquid Cyclohexane Vapourised into the Reaction Chamber

Irradiation temperature = 108°C

P = Pressure of cyclohexane vapour in mms, at 108°C

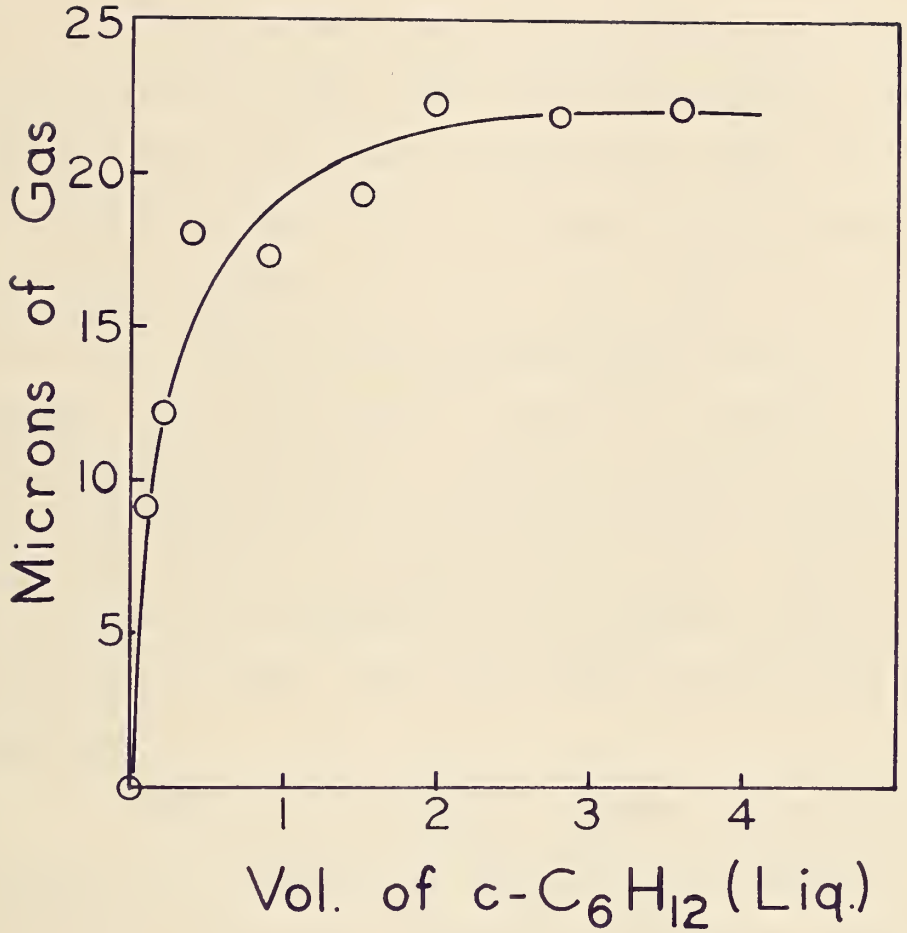
μ = Microns of gas volatile at - 196°C measured in the 546 ml volume of the Mc Leod - Toepler gauge, corrected to 0°C

	Vol. of cyclohexane (mls of liquid)	P	μ (- 196°C)
1.	0.0	0.0	0.0 (blank expt)
2.	0.1	21.5	9.1
3.	0.2	43.1	12.2
4.	0.4	76.3	18.1
5.	0.9	192.4	17.2
6.	1.5	318.4	19.3
7.	2.0	433.0	22.4
8.	2.8	599.7	21.8
9.	3.6	764.7	22.1

Figure 6

Figure 6

Yield of Gas Volatile at -196°C as a Function of the Volume of Cyclohexane Liquid Vapourised


25
20
15
10
5
Microns of Gas
1
2
3
4
Vol. of c-C6H12 (Liq.)

alpha particles when two or more mls of cyclohexane are vapourised into the reaction vessel. The size of the sample of cyclohexane employed in all subsequent experiments was two mls.

(2) Radiolysis of cyclohexane as a function of dose

Cyclohexane vapour was irradiated to various doses over the range 0.79×10^{19} ev to 15.9×10^{19} ev. The yields of the gases volatile at -196°C and -112°C are presented in Table VII and Figure 7. The average G values for gases volatile at -196°C and -112°C are approximately 8.1 ± 0.3 and 4.9 ± 0.5 respectively. It is clear from Figure 7 that the G(gas) volatile at -196°C is fairly constant while the G(gas) volatile at -112°C decreases steadily. The amount of methane was so small that it could only be detected and measured at the highest dose by the present analytical system. Thus the -196°C fraction was essentially hydrogen.

The yields of other products in the dose function studies are presented in Table VIII and Figure 8. The yields of ethane, ethylene, acetylene, propylene, cyclohexene, dicyclohexyl and the total C_{12} hydrocarbons appear to be constant. The butane peak appeared as a shoulder on the tail of the propylene peak in the chromatograms and was about

TABLE VII

Yields of the Gases Volatile at -196°C and -112°C as a Function of Dose in the Radiolysis of Cyclohexane

Irradiation temperature = 108°C

μ = microns of gas, volatile at -196°C or -112°C, measured in the 546 ml volume of the Mc Leod - Toepler gauge, blank value subtracted and then corrected to 0°C

Blank values { -196°C fraction = 5.4 microns; -112°C fraction = 9.4 microns

	Dose(ev)x10^{-19}	-196°C fraction		-112°C fraction	
		μ	G	μ	G
1.	0.79	33.5	7.9	22.9	5.6
2.	1.35	56.0	8.0	43.0	5.4
3.	1.58	68.4	8.5	36.4	4.5
4.	2.70	108.0	7.8	75.0	5.0
5.	2.90	128.5	8.5	64.3	4.0
6.	3.95	163.3	8.4	98.9	4.1
7.	4.95	204.0	7.3	136.0	4.7
8.	6.10	417.0	7.5	266.0	4.5
9.	15.90	860.0	7.7	436.0	3.8

Figure 7

Figure 7

G(-196°C) and G(-112°C) as a Function of Dose

(Cyclohexane Radiolysis)

G(-196°C) = G(gas) volatile at -196°C

G(-112°C) = G(gas) volatile at -112°C

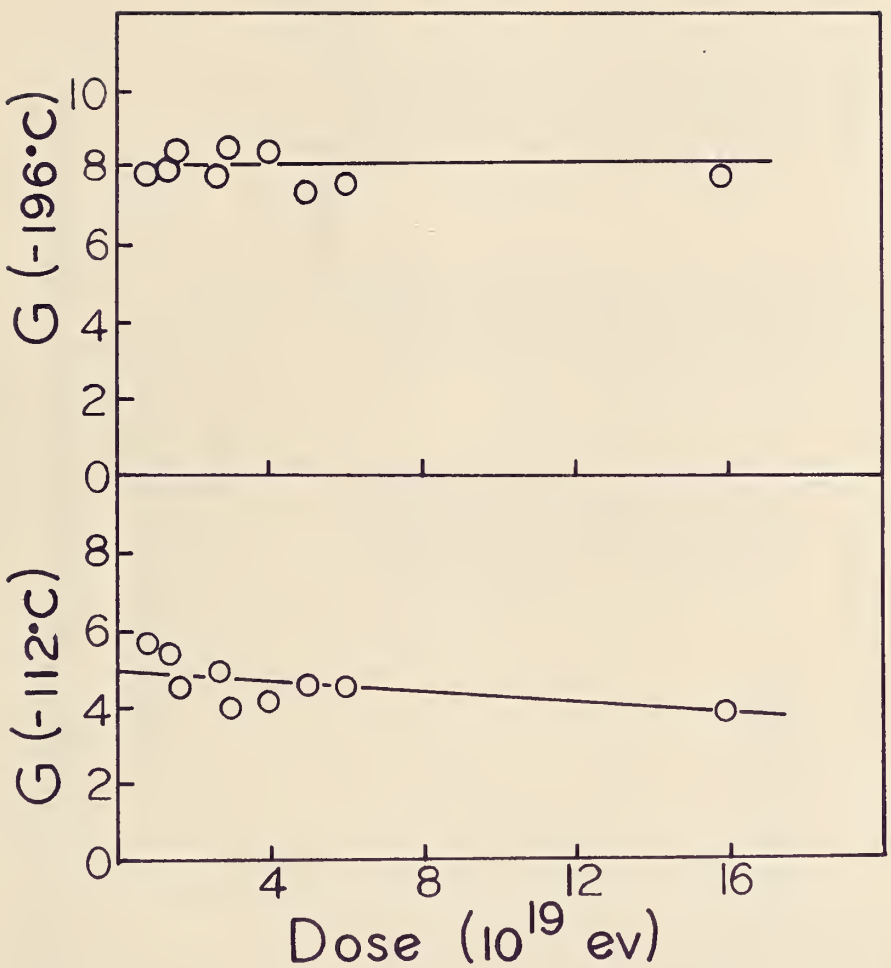

G (-196°C)
10
8
6
4
2
0
G (-112°C)
8
6
4
2
0
4
8
12
16
Dose (10^19 ev)

TABLE VIII

G (Products) of Irradiation of Cyclohexane Vapour as a Function of Dose

Irradiation Temperature = 108°C

2.5 m Silica-gel column

	Products	Dose (ev) x 10^{-19}				
		1.35	2.70	5.0	6.1	15.9
1.	C_2H_6	0.30	0.29	0.25	0.23	0.21
2.	C_2H_4	2.54	2.37	2.64	2.64	2.01
3.	C_2H_2	0.75	0.83	0.47	0.51	0.51
4.	C_3H_8	1.18	0.87	0.76	0.67	0.47
5.	$C_3H_6 + C_4H_{10}$	0.86	0.85	0.84	-	0.70
6.	C_4 olefin (probably C_4H_8)	0.37	0.47	0.48	0.49	0.98
7.	Cyclohexene	-	0.76	0.72	0.74	0.84
8.	Dicyclohexyl	-	-	0.45	0.39	0.54
9.	Total C_{12} hydrocarbons (apiezon L column)	-	-	0.84	0.57	0.65

Figure 8

Figure 8

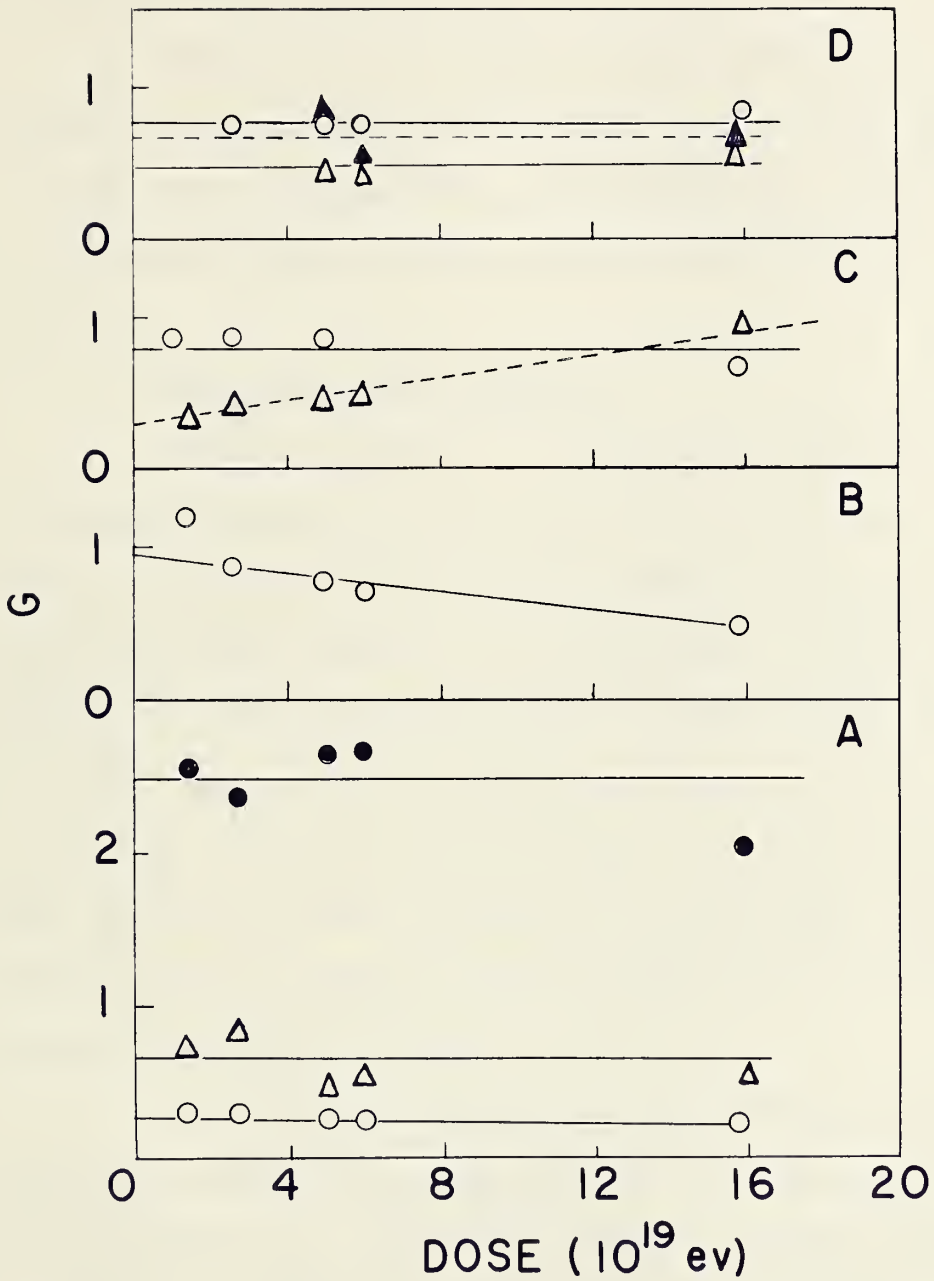
Product Yields as a Function of Dose

A. ethane
acetylene
ethylene

B. propane

C. C_4 olefin (probably C_4H_8)
propylene

D. cyclohexene
dicyclohexyl
total C_{12} hydrocarbons


D
C
B
A
G
0
1
2
0
4
8
12
16
20
DOSE (10^{19} ev)

5 percent of the propylene peak. The propane yield seems to decrease with dose while the C_4 hydrocarbon yield appears to increase.

The yields of other products obtained in the highest dose experiment are $G(CH_4) = 0.13$, $G(C_8$ hydrocarbon) $= 0.06$, $G(C_9$ hydrocarbon) $= 0.07$ and $G(C_{10}$ hydrocarbon) $= 0.17$. No detectable amount of methane was found in gases volatile at $-112^{\circ}C$.

(3) Inhibition Studies

Binary solutions of cyclohexane with the various inhibitors, benzene, cyclohexene and propylene, were irradiated for two hours. The gaseous products volatile at $-196^{\circ}C$ and $-112^{\circ}C$ were measured by the Mc Leod - Toepler gauge. The results are given in Tables IX - XI. The G(gas) non-condensable at $-112^{\circ}C$ are not very reliable and more work has to be done before any conclusions can be drawn concerning them. Since these solutions were irradiated for two hours only, sufficient liquid products did not form to permit their analysis with the present analytical system.

In the cyclohexane systems, the hydrogen yields, $G(H_2)$, are plotted as a function of the electron fraction of the inhibitor, ϵ_i . This was adopted assuming that G(gas) volatile at $-196^{\circ}C$ is equal to $G(H_2)$ since the methane yield

TABLE IX

Gaseous Yields from the Irradiation of Cyclohexane - Benzene Solutions

Irradiation temperature = 108°C

μ = microns of gas, volatile at -196°C or -112°C, measured in the 546 ml volume of the Mc Leod - Toepler gauge, corrected to 0°C

G(-196°C) or G(-112°C) = G of gas volatile at the temperature mentioned in parenthesis

ϵ = Electron fraction (no. of moles of electrons) of benzene in the solution

	Percent composition (volume percent)	ϵ (benzene)	μ(-196°C)	G(-196°C)	μ(-112°C)	G(-112°C)
1.	0.0	0.0000	113.0	8.1	76.7	5.7
2.	0.8	0.0085	110.0	7.9	68.6	4.9
3.	2.0	0.0213	99.3	7.1	64.1	4.6
4.	4.0	0.0424	81.8	5.9	62.8	4.5
5.	8.0	0.0847	68.2	4.9	79.1	5.7
6.	20.0	0.2102	49.7	3.5	56.5	4.0
7.	50.0	0.5156	30.2	2.2	52.3	3.8
8.	100.0	1.0000	20.5	1.5	40.9	2.9

TABLE X

Gaseous Yields from the Irradiation of Cyclohexane - Cyclohexene Solutions

Irradiation temperature = 108°C

μ = microns of gas, volatile at -196°C or -112°C, measured in the 546 ml volume of the Mc Leod - Toepler gauge, corrected to 0°C

G(-196°C) or G(-112°C) = G of gas volatile at the temperature mentioned in parenthesis

ϵ = Electron fraction (no. of moles of electrons) of cyclohexene in the solution

	Percent composition (volume percent)	ϵ (cyclohexene)	μ(-196°C)	G(-196°C)	μ(-112°C)	G(-112°C)
1.	0.0	0.0000	113.0	8.1	76.7	5.7
2.	0.8	0.0081	88.1	6.3	62.0	4.4
3.	2.0	0.0204	74.0	5.3	61.6	4.4
4.	4.0	0.0408	64.2	4.6	66.9	4.8
5.	8.0	0.0816	63.0	4.5	68.9	4.9
6.	20.0	0.2033	58.9	4.2	98.3	7.0
7.	50.0	0.5053	49.3	3.5	80.7	5.8
8.	100.0	1.0000	46.0	3.4	61.6	4.4

TABLE XI

Gaseous Yields from the Irradiation of Cyclohexane - Propylene Mixtures

Irradiation temperature = 108°C

μ = microns of gas, volatile at -196°C, measured in the 546 ml volume of the Mc Leod - Toepler gauge, corrected to 0°C

G(-196°C) = G of gas volatile at -196°C

ϵ = Electron fraction (no. of moles of electron) of the propylene in the mixture

	Pressure (mm) (propylene)	ϵ (propylene)	μ(-196°C)	G(-196°C)
1.	0.0	0.0000	113.0	8.1
2.	1.5	0.0017	95.9	6.9
3.	11.4	0.0136	79.5	5.7
4.	24.7	0.0292	67.0	4.8
5.	49.3	0.0592	60.3	4.3
6.	97.0	0.2169	58.7	4.2
7.	204.0	1.0000	32.3	2.34

was very small in comparison with the hydrogen yield. The electron fraction, ϵ_i, is defined by

$$\epsilon_i = \frac{E_i V_i}{E_i V_i + E_c V_c}$$

where E_i and E_c are the electron densities (number of moles of electrons per ml) of the inhibitor and of cyclohexane respectively, and V_i and V_c are their respective volumes. Table XII gives the electron densities of the materials employed in these studies. For convenience, the electron densities of methyl cyclohexane and ethanol are also included. The density values in Table XII were adopted from the book edited by Rossini et al (123).

Figure 9 contains the plots of $G(H_2)$ observed against the electron fraction of the inhibitor in the cyclohexane - propylene, cyclohexane - cyclohexene and cyclohexane - benzene systems. It can be readily seen that the hydrogen yield decreases with increase in the concentration of inhibitor. Figure 9 also makes it evident that both propylene and cyclohexene reduce the yield to a greater extent than benzene in the low concentration region. The broken lines in this figure indicate the $G(H_2)$ that might have been expected if there had been no interaction between the components of the gas mixtures and if the energy

TABLE XII

Electron Density Values for the Compounds used in the present work

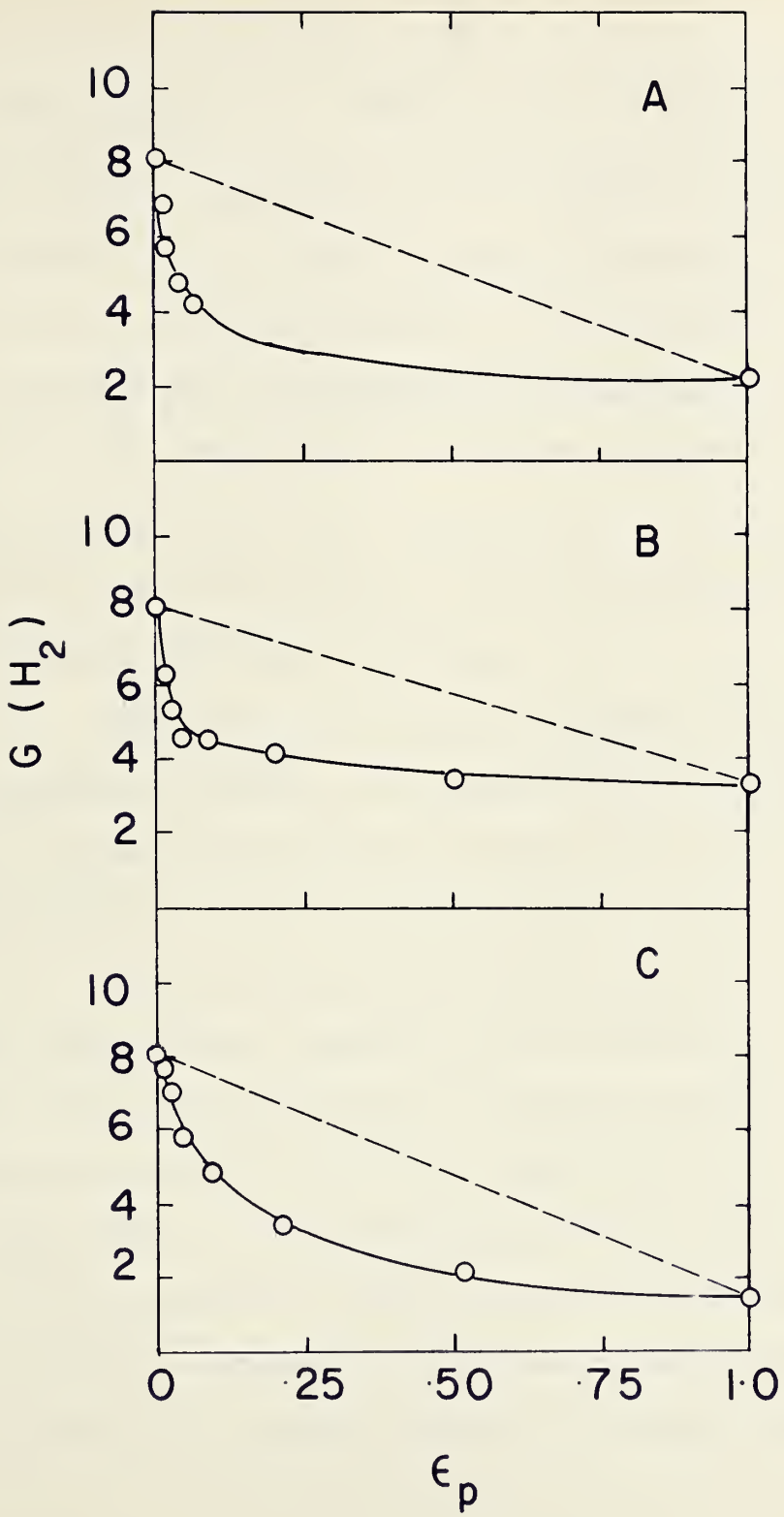
Compound	Mol.Wt.	Density at 25°C (g/ml)	E(e^- moles/ml)
1. Cyclohexane	84.16	0.774	0.441
2. Cyclohexene	82.14	0.806	0.451
3. Benzene	78.11	0.874	0.470
4. Methyl Cyclohexane	98.18	0.765	0.436
5. Ethanol	46.07	0.789	0.445

Figure 9

Figure 9

Hydrogen Yield as a Function of Protector Concentration

ϵ_P	electron fraction of protector, P
A	P = propylene
B	P = cyclohexene
C	P = benzene


A
B
C
10
8
6
4
2
G (H2)
0
·25
·50
·75
1·0
ϵp

absorption by a component were proportional to the electron fraction of the component. Thus

$$G(H_2)_{expected} = G(H_2)^{\circ}_{c} \epsilon_{c} + G(H_2)^{\circ}_{i} \epsilon_{i}$$

where $G(H_2)^{\circ}_{c}$ and $G(H_2)^{\circ}_{i}$ are the hydrogen yields for pure cyclohexane and for pure inhibitor respectively and ϵ_{c} and ϵ_{i} are the electron fractions of the respective components.

(d) Benzene, cyclohexene and propylene radiolyses

The radiolyses of benzene, cyclohexene and propylene were briefly studied as a side issue, since these were the end points in the inhibition runs of cyclohexane, methyl cyclohexane and ethanol systems.

The G values of gases volatile at -196°C from the radiolyses of benzene, cyclohexene and propylene in the two hour runs are listed along with the corresponding doses in Table XIII.

Since no liquid products could be detected at the lower doses, these compounds were irradiated with higher doses and the distributions of products thereby obtained are presented in Table XIV. The G values of the products listed in Table XIV are calculated on the basis of G values obtained for gases volatile at -196°C in the two hour run of the corresponding compound. The methane yields from benzene and cyclohexene are combined yields of methane obtained in gases

TABLE XIII

G Values of Gaseous Products Obtained in the Radiolyses of Benzene and Cyclohexene Vapours and of Propylene

Irradiation temperature = 108°C

G(-196°C) = G of gas volatile at -196°C

Substance	Dose (ev)x10^{-19}	G(-196°C)
1. Benzene	1.10	1.51
2. Cyclohexene	0.78	3.38
3. Propylene	0.63	2.34

TABLE XIV

G Values of Products from the Vapour Phase Radiolyses of Benzene, Cyclohexene and Propylene

Irradiation temperature = 108°C

	Substance		
	Benzene	Cyclohexene	Propylene
Dose(ev)x10^{-20}	1.7	3.0	1.8
Products:			
H_2	1.38	3.10	2.21
CH_4	0.13	0.28	0.13
C_2H_6	0.08	0.05	-
C_2H_4	0.07	1.55	-
C_2H_2	1.15	0.62	Trace
C_3H_6	-	0.07	-
C_3H_8	-	0.14	-
C_4 olefin	-	0.16	-
c-C_6H_{12}	-	1.35	-
C_6H_6	-	0.12	-
Total C_{12} hydrocarbons	0.31	2.65	-

volatile at -196°C and - 112°C. The yields of methane from gases volatile at -196°C in irradiations of benzene and cyclohexene were respectively about 82 percent and 85 percent of the total methane yields. The total C_{12} hydrocarbons in both benzene and cyclohexene radiolyses were obtained by using a one metre apiezon L chromatography column. In cyclohexene radiolysis, silica-gel column analysis showed the formation of dicyclohexyl (G = 0.16), cyclohexylcyclohexene (G = 0.85) and dicyclohexyl (G = 1.46). The sum of the yields of the C_{12} hydrocarbons on silica-gel column (G = 2.47) is in fair agreement with the total C_{12} hydrocarbon yield (G = 2.65) obtained on 1 metre apiezon L column.

(e) Methyl Cyclohexane radiolysis

(1) Radiolysis of methyl cyclohexane as a function of dose

The decomposition of methyl cyclohexane by Po^{210} alpha particles was investigated over the dose range from 0.31×10^{19}ev to 17.9×10^{19}ev. The yields of the gases volatile at - 196°C and - 112°C are presented in Table XV and Figure 10.

It can be seen from Figure 10 that G(gas) volatile at -196°C is fairly constant while G(gas) volatile at -112°C decreases and then levels off as the dose increases. The average G value of gases volatile at -196°C is about 6.1 ± 0.2.

TABLE XV

Yields of Gases Volatile at -196°C and -112°C as a Function of Dose in the Radiolysis of Methyl Cyclohexane

Irradiation temperature = 108°C

μ = microns of gas volatile at -196°C or -112°C, measured in the 546 ml volume of the Mc Leod - Toepler gauge, blank value subtracted and then corrected to 0°C

Blank values { -196°C fraction = 4.5 microns; -112°C fraction = 9.4 microns

	Dose (ev)x10^{-19}	μ(-196°C)	G(-196°C)	μ(-112°C)	G(-112°C)
1.	0.31	41.3	5.92	27.9	4.0
2.	0.60	88.3	6.33	41.7	3.0
3.	0.88	112.9	5.40	49.3	1.9
4.	1.20	169.4	6.07	45.7	1.6
5.	1.75	251.5	6.01	53.9	1.3
6.	17.90	6270.3	6.39	879.3	0.9

Figure 10

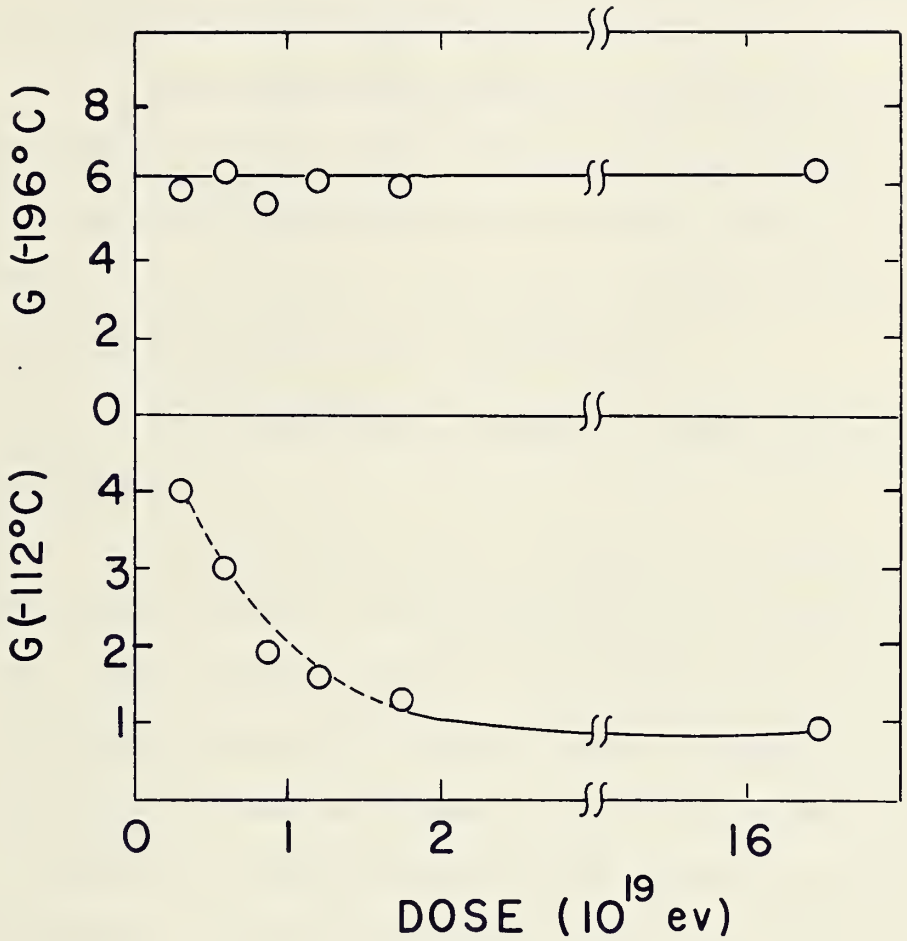
Figure 10

G(-196°C) and G(-112°C) as a Function of Dose

(Methyl cyclohexane radiolysis)

G(-196°C) = G(gas) volatile at -196°C

G(-112°C) = G(gas) volatile at -112°C


G (-196°C)
G(-112°C)
8
6
4
2
0
4
3
2
1
0
1
2
16
DOSE (10^19 ev)

The amount of methane could only be detected and measured at the three highest doses. The combined yields of methane from gases volatile at -196°C and -112°C at these doses were 0.41, 0.3 and 0.31 respectively. Of these methane yields, the amounts that were obtained from gases volatile at -196°C were correspondingly 59 percent, 67 percent and 35 percent of the total methane yield.

The individual product yields of the gases volatile at -112°C are not given, though ethane, ethylene, propane, acetylene and propylene were detected. These product yields are not very reliable. No liquid products could be detected even in the highest dose experiments.

(2) Inhibition studies of the methyl cyclohexane systems

Binary solutions of methyl cyclohexane with the inhibitors benzene and cyclohexene were radiolysed for two hours. The gaseous products non-condensable at -196°C and -112°C were measured by the Mc Leod - Toepler gauge. The results are given in Tables XVI and XVII. The G(gas) volatile at -112°C are scattered and do not appear to show any trend. The method of analysis of this fraction requires more work before it can be of any use.

Figure 11 is a plot of G(-196°C) against the electron fraction, ϵ_i, of the inhibitor. G(-196°C) was used as the

TABLE XVI

Gaseous Yields from the Irradiation of Methyl Cyclohexane - Benzene Systems

Irradiation temperature = 108°C

μ = microns of gas, volatile at -196°C or -112°C, measured in the 546 ml volume of the Mc Leod - Toepler gauge, corrected to 0°C

G(-196°C) or G(-112°C) = G of gas volatile at the temperature mentioned in parenthesis

ϵ = Electron fraction (no. of moles of electron) of benzene in the mixture

	Percent Composition (Volume percent)	ϵ (benzene)	μ(-196°C)	G(-196°C)	μ(-112°C)	G(-112°C)
1.	0.0	0.0000	51.3	6.3	18.7	2.3
2.	1.0	0.0108	47.5	5.8	17.3	2.1
3.	2.0	0.0215	44.6	5.5	15.3	1.9
4.	4.0	0.0430	47.2	5.8	21.5	2.6
5.	8.0	0.0857	43.0	5.3	18.7	2.3
6.	20.0	0.2123	36.5	4.5	27.8	3.4
7.	40.0	0.4181	20.6	2.6	19.9	2.5
8.	100.0	1.0000	20.5	1.5	38.7	3.1

TABLE XVII

Gaseous Yields from the Irradiation of Methyl Cyclohexane - Cyclohexene Systems

Irradiation temperature = 108°C

μ = microns of gas, volatile at -196°C or -112°C, measured in the 546 ml volume of the Mc Leod - Toepler gauge, corrected to 0°C

G(-196°C) or G(-112°C) = G of gas volatile at the temperature mentioned in parenthesis

ϵ = Electron fraction (no. of moles of electron) of cyclohexene in the mixture

	Percent composition (Volume percent)	ϵ (cyclohexene)	μ(-196°C)	G(-196°C)	μ(-112°C)	G(-112°C)
1.	0.0	0.0000	51.3	6.3	18.7	2.30
2.	1.0	0.0103	42.3	5.12	23.8	2.56
3.	2.0	0.0206	35.7	4.33	18.3	2.03
4.	4.0	0.0431	36.6	4.43	19.5	2.12
5.	8.0	0.0900	31.8	3.84	30.1	3.27
6.	20.0	0.2055	30.0	3.64	27.3	3.00
7.	40.0	0.4081	24.1	2.95	26.5	2.90
8.	100.0	1.0000	44.4	3.44	25.8	3.15

Figure 11

Figure 11

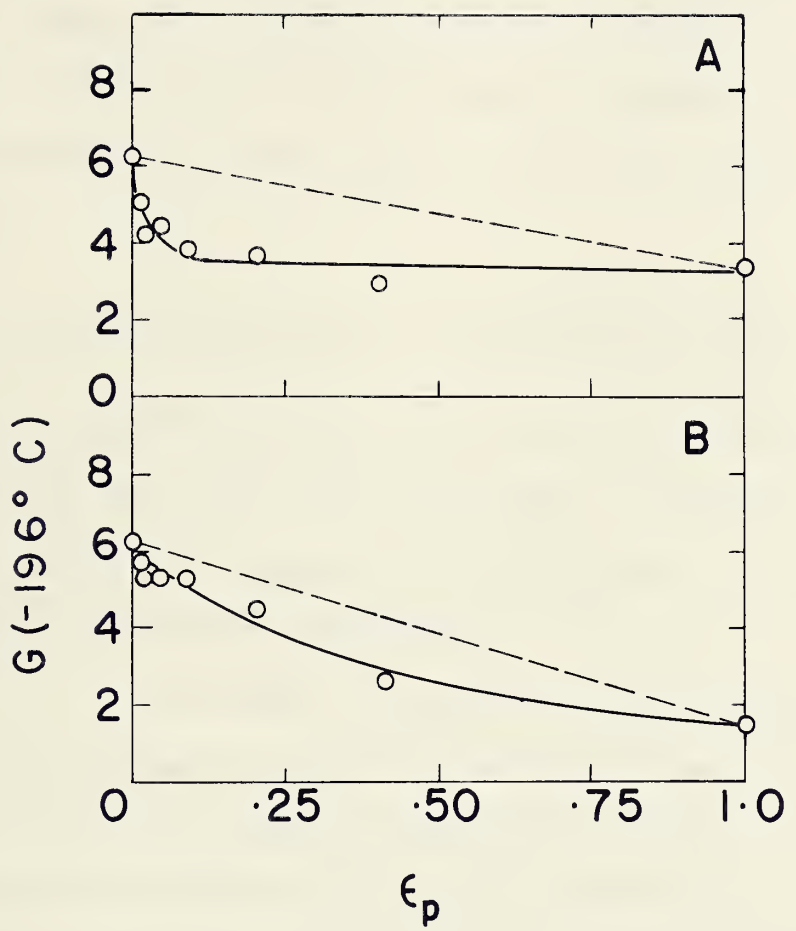
G(-196°C) as a Function of Protector Concentration

ϵ_P = electron fraction of protector, P

A: P = cyclohexene

B: P = benzene

G(-196°C) = G(gas) volatile at -196°C


A
B
8
6
4
2
0
8
6
4
2
0
·25
·50
·75
1·0
G(-196° C)
ϵ_p

ordinate instead of $G(H_2)$, because methane was an appreciable proportion of the hydrogen yield. ϵ_i is defined in the same manner as previously. The yield of the gases volatile at -196°C decreases with increase in the concentration of the inhibitor in both cases. The broken lines indicate the hydrogen yield that might have been expected if there had been no interaction between the components and if the energy absorption were directly proportional to the electron fraction of the component. Thus

$$G(-196^{\circ}C)_{expected} = G(-196^{\circ}C)^{\circ}_m \epsilon_m + G(-196^{\circ}C)^{\circ}_i \epsilon_i$$

where $G(-196^{\circ}C)^{\circ}_m$ and $G(-196^{\circ}C)^{\circ}_i$ are yields of gases volatile at -196°C for pure methyl cyclohexane and for pure inhibitor respectively and ϵ_m and ϵ_i are the corresponding electron fractions.

Although the points do not fall on a smooth curve in Figure 11, yet it can be noticed that there is a decrease in the yield of the gases volatile at -196°C with increasing concentration of the protector. The cyclohexene appears to reduce the yield to a greater extent than benzene in the low concentration region.

(f) Ethanol radiolysis

(1) Radiolysis of ethanol as a function of dose

Pure ethanol (containing about 0.005 mole percent water) was subjected to alpha radiation and the gaseous product yield distribution was studied as a function of dose, the dose range employed being 0.496×10^{19} ev to 3.77×10^{19} ev. The yields of gases volatile at -196°C and -112°C are given in Table XVIII and Figure 12. The G values of gases, non-condensable at -196°C appear to be constant over this dose range while the G values of gases, volatile at -112°C decrease with increasing dose. The average G value of gases volatile at -196°C is approximately 10.7 ± 0.4.

The products that constituted the fractions volatile at -196°C and -112°C were all measured and their G values are presented as a function of dose in Table XIX and Figure 13. The yields of methane are the combined yields obtained from the two gas fractions, volatile at -196°C and -112°C. The portion of the total methane, derived from the -196°C fraction, increased from 21 percent at the lowest dose to 58 percent at the highest dose. However, the methane yield obtained from gases volatile at -196°C remained approximately constant, with a G of 1.1 ± 0.1 except for the lowest dose experiment.

It can be seen in Figure 13 that methane, carbon monoxide and ethylene decrease more rapidly with increasing dose than do others.

TABLE XVIII

Yields of Gases Volatile at -196°C and -112°C as a Function of Dose in the Radiolysis of Ethanol

Irradiation temperature = 108°C

μ = microns of gas, volatile at -196°C or -112°C, measured in the 546 ml volume of the Mc Leod - Toepler gauge, blank value subtracted and then corrected to 0°C

Blank values { -196°C fraction = 2.8 microns; -112°C fraction = 1.7 microns

	Dose (ev)x10^{-19}	μ(-196°C)	G(-196°C)	μ(-112°C)	G(-112°C)
1.	0.496	31.8	10.6	10.7	3.6
2.	0.979	62.7	10.5	24.4	4.0
3.	2.162	124.7	10.4	31.2	2.6
4.	3.162	195.9	10.8	35.8	2.0
5.	3.765	270.1	11.2	40.0	1.7

Figure 12

Figure 12

G(-196°C) and G(-112°C) as a Function of Dose

(Ethanol radiolysis)

G(-196°C) = G(gas) volatile at -196°C

G(-112°C) = G(gas) volatile at -112°C

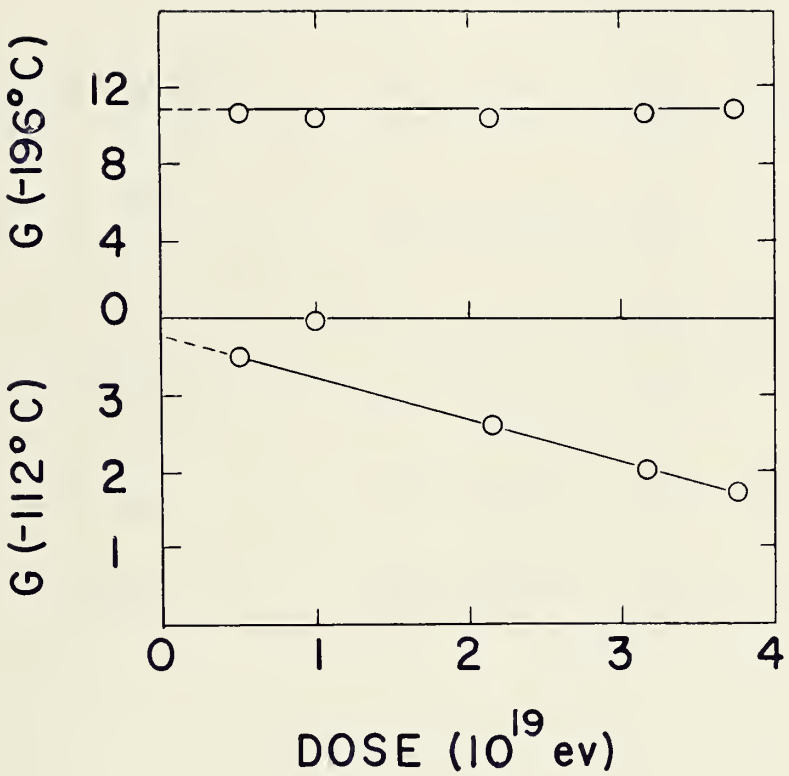

G (-196° C)
G (-112° C)
12
8
4
0
3
2
1
0
1
2
3
4
DOSE (10^{19} ev)

TABLE XIX

G Values of Gases Volatile at -196°C and -112°C as a Function of Dose

Ethanol irradiations

Irradiation temperature = 108°C

	Dose (ev)x10^{-19}	H_2	CO	CH_4	C_2H_6	C_2H_4
1.	0.496	9.2	0.90	2.4	0.24	1.43
2.	0.979	8.2	0.99	3.53	0.30	1.40
3.	2.162	8.6	0.84	2.09	0.12	1.35
4.	3.162	9.0	0.75	2.00	0.11	0.98
5.	3.765	9.5	0.65	1.70	0.17	0.82

Figure 13

Figure 13

G Values of Products Volatile at -196°C and -112°C in the Dose Function Experiments of Ethanol

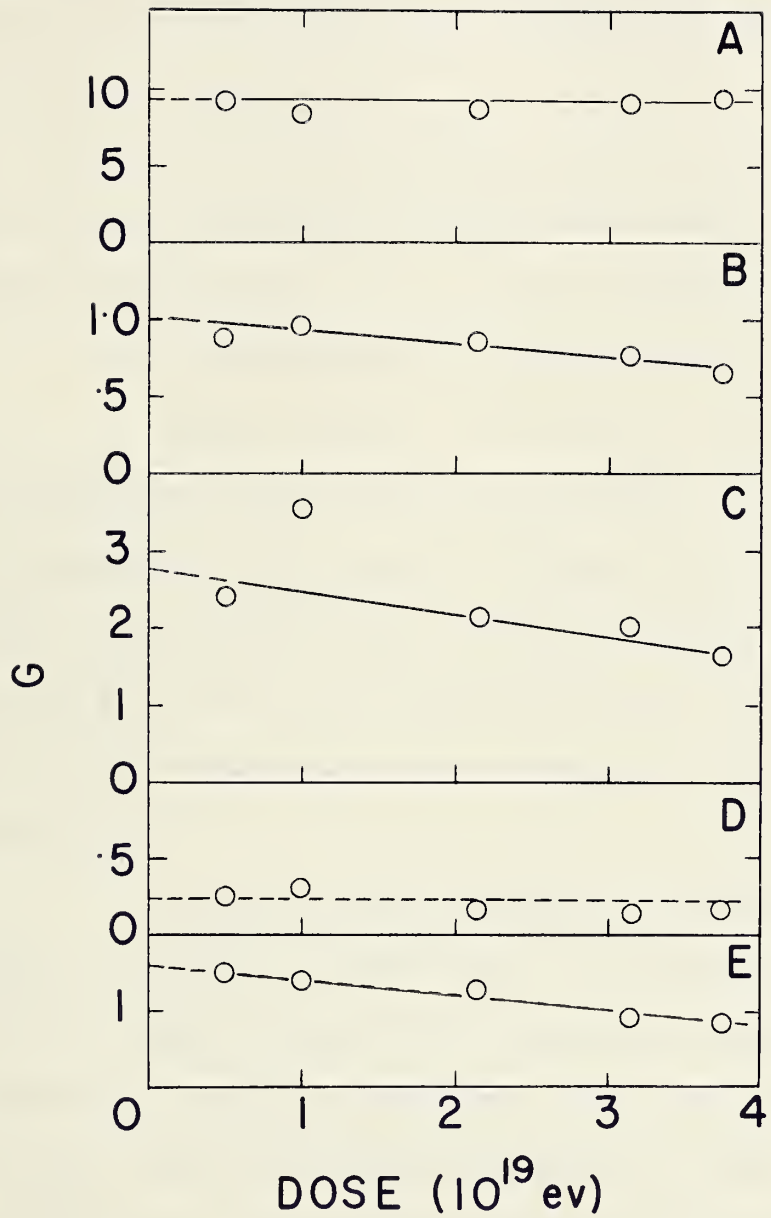
A : hydrogen

B : carbon monoxide

C : methane

D : ethane

E : ethylene


A
B
C
D
E
10
5
0
1·0
·5
0
3
2
1
0
·5
0
1
0
G
0
1
2
3
4
DOSE (10^{19} ev)

Since no measurable amounts of liquid products were obtained in these dose function experiments, an appreciably higher dose, 12.7×10^{20} ev, was given to an ethanol sample and the liquid products were measured. These are given in Table XX along with the gaseous products obtained at the same dose.

The yield of water seems to be abnormally high. There is fair agreement between the total glycols (ucon column) and the sum of the vicinal glycols (carbowax column).

(2) Inhibition studies of the ethanol systems

Binary vapour solutions of ethanol with benzene or cyclohexene were irradiated by Po^{210} alpha particles for two hours each. The gaseous products volatile at $-196^{\circ}C$ and $-112^{\circ}C$ were measured. The results are summarised in Tables XXI and XXII. Since the results of the yields of gases volatile at $-112^{\circ}C$ were very irregular, they have been omitted.

In Tables XXI and XXII, the yield from pure ethanol is slightly higher than in the dose function experiments. Since these were a series of experiments, all the other values would be relative. Hence the experimentally obtained G value for gases volatile at $-196^{\circ}C$ in this series for pure ethanol was used for the kinetic analysis.

Figure 14 is a plot of the G of gases volatile

TABLE XX

G Values of the Various Products Obtained by Irradiating Ethanol

Irradiation temperature = 108°C

Dose (ev) x 10^{-20} = 12.7

	Product	G
1.	Hydrogen	7.6
2.	Carbon monoxide	1.1
3.	Methane	1.66
4.	Ethane	0.23
5.	Ethylene	0.72
6.	Acetylene	0.03
7.	C_3 and C_4 hydrocarbons	Trace
8.	Water	5.4
9.	Formaldehyde	0.9
10.	Acetaldehyde	4.5
11.	Propanol	0.6
12.	Butanol	0.19
13.	1,2 Propane diol	0.15
14.	2,3 Butane diol	1.2
15.	Total glycols(ucon column)	1.6

TABLE XXI

Gaseous Yields from the Irradiation of the Ethanol - Benzene Systems

Irradiation temperature = 108°C

μ = microns of gas, volatile at -196°C, measured in the 546 ml volume of the Mc Leod - Toepler gauge, corrected to 0°C

G(-196°C) = G(gas) volatile at -196°C

ϵ = Electron fraction (no. of moles of electron) of benzene in the mixture

	Percent composition (Volume percent)	ϵ (benzene)	μ(-196°C)	G(-196°C)
1.	0.0	0.0000	133.4	11.2
2.	2.0	0.0211	129.8	10.9
3.	4.0	0.0415	125.9	10.6
4.	8.0	0.0842	99.6	8.4
5.	20.0	0.1961	72.1	6.1
6.	50.0	0.5139	33.3	2.8
7.	100.0	1.0000	20.5	1.5

TABLE XXII

Gaseous Yields from the Irradiation of Ethanol - Cyclohexene Systems

Irradiation temperature = 108°C

μ = microns of gas volatile at -196°C, measured in the 546 ml volume of the Mc Leod - Toepler gauge, corrected to 0°C

G(-196°C) = G(gas) volatile at -196°C

ϵ = Electron fraction (no. of moles of electron) of cyclohexene in the mixture

	Percent composition (Volume percent)	ϵ(cyclohexene)	μ(-196°C)	G(-196°C)
1.	0.0	0.0000	133.4	11.20
2.	1.0	0.0101	98.3	8.44
3.	2.0	0.0202	82.2	7.11
4.	4.0	0.0406	69.4	5.97
5.	8.0	0.0810	55.5	4.80
6.	20.0	0.1897	44.9	3.90
7.	50.0	0.5034	38.9	3.40
8.	100.0	1.0000	39.8	3.38

Figure 14

Figure 14

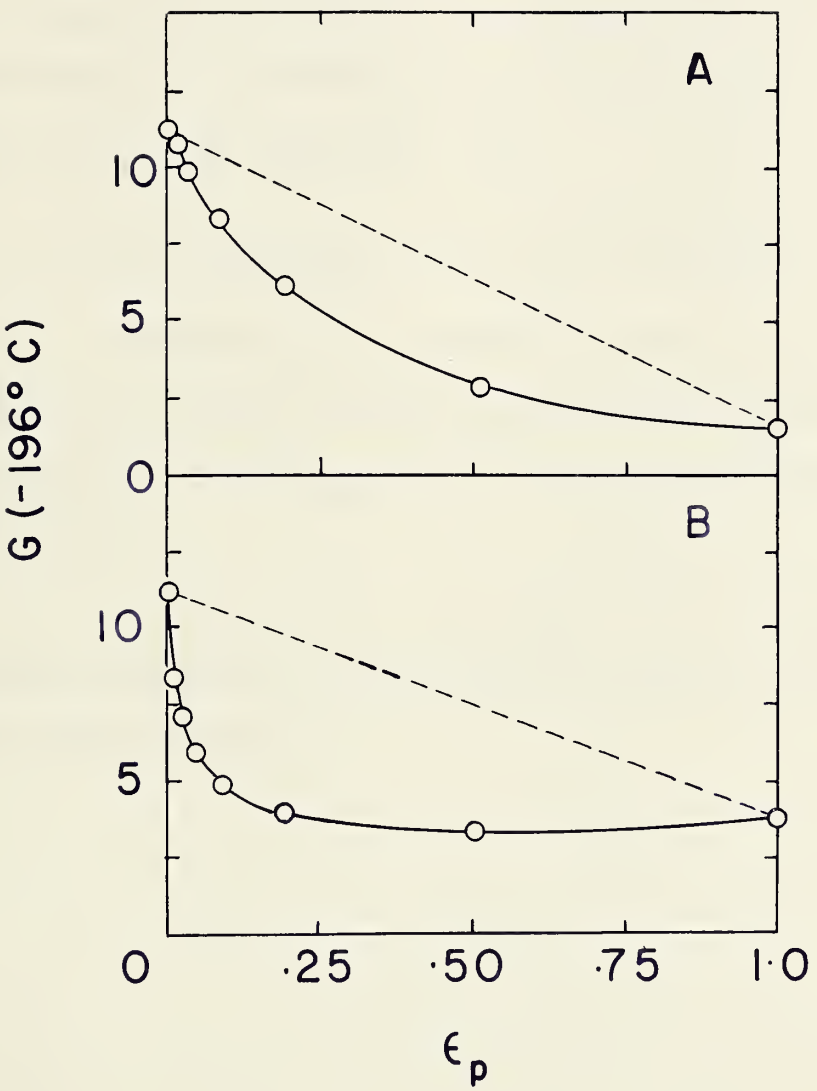
G(-196°C) as a function of Protector Concentration

$G(-196^{\circ}C)$ = G(gas) volatile at $-196^{\circ}C$

ϵ_p = electron fraction of protector, P

A: P = benzene

B: P = cyclohexene


A
B
10
5
0
10
5
0
·25
·50
·75
1·0
G (-196° C)
ϵ_p

at -196°C against the electron fraction, ϵ_i, of the inhibitor. The yield of the gases, non-condensable at -196°C decreases with increasing inhibitor concentration in both the systems. The broken lines indicate the hydrogen yield that might have been expected if there had been no interaction between the components and if the energy absorption were directly proportional to the electron fraction of the component. Thus

$$G(-196^{\circ}C)_{expected} = G(-196^{\circ}C)^{\circ}_E \epsilon_E + G(-196^{\circ}C)^{\circ}_i \epsilon_i$$

where $G(-196^{\circ}C)^{\circ}_E$ and $G(-196^{\circ}C)^{\circ}_i$ are the yields of gases volatile at -196°C for pure ethanol and for pure inhibitor respectively and ϵ_E and ϵ_i are the respective electron fractions.

It is clear from Figure 14 that cyclohexene reduces the yield of the (-196°C) fraction more rapidly than does benzene.

IV DISCUSSION

This chapter is divided into four main sections. The first deals with the radiolytic decomposition of cyclohexane and its binary solutions with benzene, cyclohexene and propylene. Since, benzene, cyclohexene and propylene were the end points in the radiolysis curves for the binary solutions, their radiolytic decomposition was briefly studied as a side issue and the second section pertains to their decomposition. The third section deals with the irradiation of methyl cyclohexane and its binary solutions. The last section is concerned with the decomposition of pure ethanol and its binary solutions with benzene and cyclohexene.

(A) Cyclohexane and its Binary Solutions

(a) Pure cyclohexane

The range of an alpha particle in a medium is roughly inversely proportional to the density of the medium. It was necessary to determine the minimum amount of cyclohexane vapour in the reaction vessel that would absorb all the energy of the alpha particles from the Po^{210} source. Figure 6 shows the results of this investigation. The initial ascending part of the curve indicates that all the alpha

particles are not absorbed completely at low cyclohexane pressures, while the plateau region, commencing when about two mls of liquid cyclohexane are used, indicated the absorption of all the alpha particles. All the subsequent investigations were therefore carried out with two mls of liquids, thereby attaining the maximum possible absorption of energy.

It appears from a general survey that hydrogen is the major single product that is obtained during the radiolysis of cyclohexane in both the liquid and gas phases. The $G(H_2)$ values obtained by various workers for liquid cyclohexane are mostly around 5.4 (58). The two values previously reported for $G(H_2)$ for vapour phase radiolysis of cyclohexane are at variance. The $G(H_2)$ for electron radiolysis of cyclohexane vapour reported by Manion and Burton (43) is 1.4 and that reported by Henri and coworkers (73) for alpha radiolysis of cyclohexane vapour is 3.6. Both these values are far lower than the corresponding values of $G(H_2)$ obtained from the radiolysis of liquid cyclohexane. This does not seem reasonable by comparison with n-pentane and n-hexane (80,124) where the gas phase yields are greater than the liquid phase yields. The true 'G' value for vapour phase cyclohexane radiolysis might be expected to be higher than those given above. In

the present work, the initial yield, $G(-196^{\circ}C)_i$, is 8.1 (Figure 7). If it is assumed that $G(CH_4) = 0.13$ at all the doses in the dose function experiments of cyclohexane, then $G(H_2)_i = 8.0$. The value of $G(-196^{\circ}C)_i$ was obtained by extrapolating the $G(-196^{\circ}C)$ values in Figure 7 to zero dose.

The product distribution in the radiolysis of cyclohexane vapour was studied as a function of dose. The yield of gases volatile at $-196^{\circ}C$ is a linear function of dose over the range studied. It can therefore be suggested that the primary decomposition of excited cyclohexane vapour molecules is linearly dependent on dose. The decrease in the yields of some of the products is probably due to secondary reactions. The absorption of 10^{20} ev would correspond to the decomposition of about 0.1 percent of the cyclohexane.

If the decomposition of cyclohexane vapour is represented as

$$c\text{-}C_6H_{12} \longrightarrow H_2 + X$$

then the total hydrogen deficiency in the initial yields of the products X should be equal to $G(H_2)_i = 8.0$. A material balance of all the products measured during the radiolysis of cyclohexane is given in Table XXIII. The C_8, C_9 and C_{10} hydrocarbons may be secondary products and perhaps should not have been included in the table. Since no G_i values were available for these compounds, the G values

TABLE XXIII

Material Balance of Products from Irradiation of Cyclohexane Vapour

The hydrogen equivalent of a product corresponds to the amount of hydrogen that was formed when that product was formed from cyclohexane

Product	G_i	H_2 equivalent
C_2H_6	0.28	0.28
C_2H_4	2.48	0.00
C_2H_2	0.65	0.65
C_3H_8	0.95	0.95
C_3H_6	0.78	0.00
C_4H_{10}	0.04	0.04
C_4H_8	0.30	0.00
Cyclohexene	0.77	0.77
C_8 hydrocarbon	(0.06)	(0.06?)
C_9 hydrocarbon	(0.07)	(0.07?)
C_{10} hydrocarbon	(0.17)	(0.17?)
Total C_{12} hydrocarbons	0.69	0.69
	Total	1.14
H_2	8.0	8.0

obtained in the highest dose run are given and are in parenthesis.

It can be easily seen, by comparing the total hydrogen equivalent of the hydrocarbon products with $G(H_2)_i = 8.0$, that the hydrogen equivalent of about 7 G units of hydrocarbon products have been missed. A similar deficiency of over one G unit in material balance has been reported by Freeman (58) in the liquid phase radiolysis of cyclohexane. The analysis of the products was performed by Freeman using vapour phase chromatography. The only instance where a good material balance was obtained was in a study of the effect of quinones on the γ-radiolysis of liquid cyclohexane (125).

From the investigation of the alpha radiolysis of cyclohexane vapour, Henri and coworkers (73) have given the following G values of the products: $H_2 = 3.6$; $CH_4 = 0.53$; $C_2H_6 = 1.2$; $C_3H_8 = 0.33$; $C_4H_{10} = 0.34$. No yields for liquid products were reported. However, it is evident that there is a very poor material balance, since the C/H ratio in all the reported hydrocarbon products is lower than that in cyclohexane.

The material balance is much worse in the vapour phase than in the liquid phase. This poor material balance might possibly be explained by ion-molecule reactions. In

that connection, an attempt was made to calculate the life time of the positive ions under the experimental conditions of this investigation.

The effective volume of cyclohexane vapour which was directly irradiated in the one litre bulb was approximately 400 ml. Assuming the value of W to be equal to 30 ev per ion pair produced, the number of ion pairs produced per cc per second by an energy input of about 10^{19} ev per hour was calculated to be 2.5×10^{11}.

From steady state treatment of the reactions

$$M \rightsquigarrow M^{+} + e \qquad \text{--(1)}$$

$$M^{+} + e \longrightarrow M^{*} \qquad \text{--(2)}$$

where M = reactant molecule, M^{+} = molecule ion, M^{*} = excited molecule, it can be written that

$$\frac{d(M^{*})}{dt} = 0 = I - k_2 (M^{+}) (e) \qquad \text{--(3)}$$

Using equation (3) and the values $k_2 \simeq 10^{-6}$ cc per ion sec.(126) and $I \simeq 2.5 \times 10^{11}$ ion per cc sec., the steady state value of $(M^{+}) \simeq 5 \times 10^{8}$ ion per cc was obtained. The mean life time, τ, of the ions would then be given by $\tau = (M^{+})/I \simeq 2 \times 10^{-3}$ sec. If another value of $k_2 \simeq 10^{-8}$ cc per ion sec.(127) is used, the values $(M^{+}) \simeq 5 \times 10^{9}$ ion

per cc and $\tau \simeq 2 \times 10^{-2}$ sec. are obtained. Thus the life time of the positive ion may be of the order of several milliseconds. However, it is believed that the life time of a positive ion in an irradiated liquid is of the order of 10^{-13} seconds (128). In view of the long life time of the positive ion in the gas phase, the carbon deficiency in the measured products may possibly be explained in terms of polymer formation by ion molecule reactions. Hydrocarbons with carbon number higher than 12 (i.e. larger than dimers of cyclohexane) would not have been detected by the present analytical system. The much longer life time of the ions in the gas phase than in the liquid phase might permit a larger amount of some such polymerisation to occur in the gas phase.

The formation of hydrogen involves the cleavage of C - H bonds in the cyclohexane molecule. The products volatile at -112°C, Viz., C_2, C_3 and C_4 hydrocarbons, involve the rupture of the ring. The acetylene might be produced by dehydrogenation of ethylene (e.g., $C_2H_4^* \longrightarrow C_2H_2 + H_2$) and the saturated hydrocarbons might be formed by hydrogenation of the olefins. The yields of the C_2, C_3 and C_4 hydrocarbon products were over ten times greater in the gas phase than they were in the liquid phase irradiations (58). This large difference might be due to the rapid recombination

of hydrocarbon radical fragments in the liquid cages. It might also be partly due to the formation of different excited species in the two phases.

If hydrogen is formed by the decomposition of excited cyclohexane molecules, it is probably formed by the reactions

$$c\text{-}C_6H_{12}^{*} \longrightarrow H + c\text{-}C_6H_{11} \qquad \text{--(4)}$$

$$H + c\text{-}C_6H_{12} \longrightarrow H_2 + c\text{-}C_6H_{11} \qquad \text{--(5)}$$

and possibly

$$c\text{-}C_6H_{12}^{*} \longrightarrow H_2 + c\text{-}C_6H_{10} \qquad \text{--(6)}$$

If hydrogen is produced via ion molecule reactions, these might be

$$c\text{-}C_6H_{12}^{+} + c\text{-}C_6H_{12} \longrightarrow c\text{-}C_6H_{13}^{+} + c\text{-}C_6H_{11} \qquad \text{--(7)}$$

$$c\text{-}C_6H_{13}^{+} + e \longrightarrow c\text{-}C_6H_{11} + H_2 \qquad \text{--(8)}$$

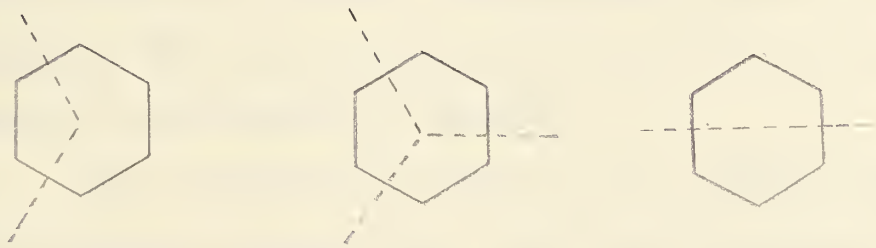
Reaction (8) represents the dissociative combination of an electron, e, with the $c\text{-}C_6H_{13}^{+}$ ion. Reactions (7) and (8) generate cyclohexyl radicals, so they are the ionic analogues of reactions (4) and (5). The cyclohexyl radicals would combine or disproportionate:

$$2\ c\text{-}C_6H_{11}^{*} \longrightarrow C_{12}H_{22} \qquad \text{--(9)}$$

$$\longrightarrow c\text{-}C_6H_{10} + c\text{-}C_6H_{12} \qquad \text{--(10)}$$

The value of the ratio of the initial yields of cyclohexene and dicyclohexyl is $G(c\text{-}C_6H_{10})_i / G(c\text{-}C_{12}H_{22})_i = 0.77/0.46 = 1.67$ which is similar to the value 1.84 observed in the liquid phase (58). This might be taken as an additional argument that only a small portion of the cyclohexene is formed by reaction (6) and that the value of the ratio k_{10} / k_9 is greater than unity in both the liquid and gas phases (129).

Ring fragmentation appears to occur in three ways:



I II III

Type II might be a continuation of type I. From the yields of C_2, C_3 and C_4 hydrocarbons, the G values for cyclohexane fragmentation of types I, II and III were calculated to be 0.3, 1.0 and 0.9 respectively. The total G value of cyclohexane molecules that underwent fragmentation was about 2.2.

The yield of propane is surprisingly high and the mechanism of its formation is not evident. The relative yields of propane and propylene indicate that the former was probably not entirely produced by hydrogenation of the latter.

(b) Inhibition experiments

The study of binary systems has helped considerably in the investigation of the primary chemical processes involved in radiation chemistry. When a solute is dissolved in a solvent and the solution irradiated, the yields of the products are frequently quite different than they would have been if the substances had been irradiated separately. If the solvent products yields are lowered, the solute is said to "protect" the solvent. Thus the amount of hydrogen from cyclohexane irradiation is considerably lowered by the presence of benzene.

Such a protective action of the solute might be caused either by trapping the free radicals produced from the primarily excited and ionised molecules or by trapping the energy from these molecules.

The aim in these investigations was to study the protection role played by benzene, cyclohexene and propylene in the decomposition of cyclohexane during irradiation in the vapour phase.

As stated by Manion and Burton (43), it might be expected that, if there were no interaction between the components of the solution, the cyclohexane product yields would be directly proportional to the fraction of the absorbed energy that is absorbed directly by the cyclohexane. It has been assumed, for lack of a better function, that the amount of energy absorbed in primary processes in a given component is directly proportional to the electron fraction, ϵ, of that component in the system.

The above assumption is probably not strictly correct because most of the ionisations and excitations in radiolytic systems are produced by electrons of about 100 ev or less energy. At these energies, the inner shell electrons (1 s electrons in carbon) will not contribute appreciably and the probability that a molecule will be ionised by electron impact will be roughly proportional to the number of outer shell electrons (valence electrons in hydrocarbons) in the molecule. Thus, for example, in the case of benzene, the outer shell electron fraction, V_b, in a solution of cyclohexane could be defined as

$$V_b = \frac{30\, n_b}{30\, n_b + 36\, n_c}$$

as compared to ϵ_b, the "total electron" fraction,

$$\epsilon_b = \frac{42\ n_b}{42\ n_b + 48\ n_c}$$

where 30 and 42 are the numbers of outer shell electrons and total electrons in benzene, 36 and 48 are the numbers of outer shell electrons and total electrons in cyclohexane; n_b and n_c are the respective number of moles of the compounds in the solution. It can be seen from the above that the values of V_b would be a bit smaller than the corresponding values of ϵ_b. However, the rate of energy loss of an energetic electron in a medium is larger, the smaller is the ionisation potential of the medium (130). The lower ionisation potential of the π electrons in benzene would lower the average ionisation potential of the outer shell electrons in benzene below that of the outer shell electrons in cyclohexane. The net effect would be to increase the relative energy absorption of benzene in the cyclohexane-benzene solutions. The lower excitation potentials of benzene would have a similar effect, especially when the energy of the exciting electrons has been degraded to a few ev. Thus the fraction of the energy absorbed by benzene may be greater than V_b. Since ϵ_b is greater than V_b, ϵ_b has been used in treating the present results.

Similar treatments can be extended to cyclohexene and propylene and ϵ_i can be shown greater than V_i, where the subscript i refers to the inhibitor (alternately called the protector).

The experimental results obtained in the inhibition experiments of cyclohexane were tested against several mechanisms and two mechanisms were found to give straight line plots. One mechanism involved scavenging of hydrogen atoms and the other involved energy transfer from cyclohexane to the protector. The two mechanisms will be treated separately.

(1) Scavenging mechanism

$$c\text{-}C_6H_{12} \xrightarrow{I} C_6H_{12}^{*} \qquad \text{--(1)}$$

$$c\text{-}C_6H_{12}^{*} \longrightarrow H + C_6H_{11} \qquad \text{--(2)}$$

$$H + c\text{-}C_6H_{12} \longrightarrow H_2 + C_6H_{11} \qquad \text{--(3)}$$

$$H + P \longrightarrow PH \qquad \text{--(4)}$$

$$H + P \longrightarrow H_2 + P\text{-} \qquad \text{--(5)}$$

In the above equations, P represents a protector such as benzene, cyclohexene or propylene, and PH and P- represent the corresponding radicals.

Since the kinetic treatment is based on the

hydrogen yield and since the formation of the other products does not appreciably affect the hydrogen yield under the present conditions, the steps for the formation of other products have not been included. It may, however, be mentioned that a detailed mechanism involving some of the other products has been given by Freeman for the liquid phase γ-radiolysis of cyclohexane-benzene (58) and cyclohexane-cyclohexene (61) systems.

By steady state treatment of the above mentioned scavenging mechanism, it can be shown that

$$\frac{d(H_2)}{dt} = k_3(H)(C_6H_{12}) + k_5(H)(P) \qquad \text{--(i)}$$

$$\frac{d(H)}{dt} = k_2(C_6H_{12}) - k_3(H)(P) - k_4(H)(P) - k_5(H)(P) = 0 \qquad \text{--(ii)}$$

$$\frac{d(C_6H_{12}^{*})}{dt} = I - k_2(C_6H_{12}^{*}) = 0 \qquad \text{--(iii)}$$

From the above equations (i), (ii) and (iii), equation (iv) can be obtained.

$$\frac{d(H_2)}{dt} = \frac{I\left[k_3(C_6H_{12}) + k_5(P)\right]}{k_3(C_6H_{12}) + (k_4 + k_5)(P)} \qquad \text{--(iv)}$$

Grouping terms in equation (iv) yields

$$\frac{d(H_2)}{dt} = I \left\{ \frac{1 + k_5(P)/k_3(C_6H_{12})}{1 + (k_4+k_5)(P)/k_3(C_6H_{12})} \right\} \quad --(v)$$

By rearrangement, equation (v) gives

$$\left\{ 1 + w \frac{(P)}{(C_6H_{12})} \right\} \frac{I}{d(H_2)/dt} = 1 + v \frac{(P)}{(C_6H_{12})} \quad --(vi)$$

$$= \rho$$

where $w = k_5/k_3$, $v = (k_4+k_5)/k_3$ and ρ represents the left hand side of equation (vi).

To obtain the values for $I / \frac{dH_2}{dt}$, the following procedure was followed. Since the yield is proportional to the energy absorbed, $I = G(H_2)^\circ_c$ for pure cyclohexane. In the presence of benzene,

$$I = G(H_2)^\circ_c \epsilon_c \quad --(vii)$$

As mentioned earlier (page 87 of this thesis)

$$G(H_2)^\circ_{expected} = G(H_2)^\circ_c \epsilon_c + G(H_2)^\circ_P \epsilon_P \quad --(viii)$$

where the symbol P replaces i in the earlier equation.

It follows from equations (vii) and (viii) that

$$I = G(H_2)^\circ_{expected} - G(H_2)^\circ_P \epsilon_P \quad --(ix)$$

Similarly, it can be written that

$$\frac{d(H_2)}{dt} = G(H_2)^{\circ}_{observed} - G(H_2)^{\circ}_{P}\,\epsilon_{P} \qquad --(x)$$

since only hydrogen production from cyclohexane is being considered.

Then

$$\frac{I}{d(H_2)/dt} = \frac{G(H_2)^{\circ}_{expected} - G(H_2)^{\circ}_{P}\,\epsilon_{P}}{G(H_2)^{\circ}_{observed} - G(H_2)^{\circ}_{P}\,\epsilon_{P}} \qquad --(xi)$$

The numerical values for $I / \frac{dH_2}{dt}$ were determined using the experimental data and equation (xi). These values are presented in Tables XXIV - XXVI.

By giving arbitrary values to w in equation (vi), sets of values of ρ were calculated. These sets of values of ρ were plotted against $(P) / (C_6H_{12})$ to see if a straight line could be obtained for each of benzene, cyclohexene and propylene. Such a line was obtained in each case (see Tables XXIV - XXVI and Figure 15) with intercept unity in accordance with equation (vi). The slope of the straight line is equal to $(k_4 + k_5) / k_3$.

The values of the various ratios of rate constants derived from these plots are shown in Table XXVII. These

TABLE XXIV

Data for the Curve Fitting the Hydrogen Yield in Cyclohexane-Benzene Systems

Scavenging mechanism w = 2.5 b = benzene c = cyclohexane

1 ϵ_b	2 $G(H_2)_{obs}$	3 (b)/(c)	4 $I = 8.1\epsilon_c$	5 $G(H_2)^{\circ}_b \epsilon_b$	6 (2-5)*	7 (4/6)* = I/ dH_2/dt	8 $1 + w\frac{(b)}{(c)}$	9 ρ = (7 x 8)*
0.0000	8.10	0.0000	8.10	0.000	8.10	1.00	1.000	1.00
0.0085	7.90	0.0098	8.03	0.013	7.89	1.02	1.025	1.05
0.0213	7.14	0.0248	7.92	0.032	7.11	1.11	1.062	1.18
0.0424	5.90	0.0574	7.76	0.061	5.84	1.33	1.144	1.52
0.0847	4.90	0.1059	7.45	0.128	4.77	1.56	1.265	1.97
0.2102	3.52	0.3043	6.41	0.318	3.20	2.00	1.761	3.52
0.5156	2.17	1.2174	3.92	0.779	1.39	2.82	4.043	11.40
1.0000	1.51	-	-	1.510	-	-	-	-

* These numbers refer to the number of the column, e.g., (2-5) means column (2) - column (5)

TABLE XXV

Data for the Curve Fitting the Hydrogen Yield in Cyclohexane-Cyclohexene Systems

Scavenging mechanism w = 25 o = cyclohexene c = cyclohexane

1 ϵ_o	2 $G(H_2)_{obs}$	3 (o)/(c)	4 $I = 8.1\epsilon_c$	5 $G(H_2)^\circ_o \epsilon_o$	6 (2-5)*	7 (4/6)* $= I/\ dH_2/dt$	8 $1 + w\frac{(o)}{(c)}$	9 $\rho = (7 \times 8)$*
0.0000	8.10	0.0000	8.10	0.000	8.10	1.00	1.000	1.00
0.0081	6.32	0.0086	8.03	0.027	6.29	1.28	1.215	1.56
0.0204	5.31	0.0218	7.93	0.069	5.24	1.51	1.545	2.33
0.0408	4.60	0.0422	7.77	0.138	4.46	1.74	2.055	3.58
0.0816	4.52	0.0928	7.44	0.276	4.24	1.75	3.320	5.81
0.2033	4.23	0.2666	6.45	0.687	3.54	1.82	7.665	13.95
0.5053	3.53	1.0663	4.01	1.708	1.83	2.19	27.658	60.57
1.0000	3.38	-	-	3.380	-	-	-	-

* These numbers refer to the number of the column, e.g., (2-5) means column (2) - column (5)

TABLE XXVI

Data for the Curve Fitting the Hydrogen Yield in Cyclohexane-Propylene Systems

Scavenging mechanism w = 10 p = propylene c = cyclohexane

1 ϵ_p	2 $G(H_2)_{obs}$	3 (p)/(c)	4 $I = 8.1\epsilon_c$	5 $G(H_2)^{\circ}_p \epsilon_p$	6 (2-5)*	7 (4/6)* $= I/dH_2/dt$	8 $I + w\frac{(p)}{(c)}$	9 $f = (7 \times 8)$*
0.0000	8.10	0.0000	8.10	0.000	8.10	1.00	1.000	1.00
0.0017	6.90	0.0035	8.09	0.004	6.90	1.17	1.035	1.21
0.0136	5.70	0.0276	7.99	0.032	5.67	1.41	1.276	1.80
0.0292	4.80	0.0655	7.87	0.068	4.73	1.66	1.655	2.75
0.0592	4.32	0.1254	7.62	0.139	4.18	1.82	2.254	4.1
0.2169	4.23	0.5607	6.35	0.508	3.72	1.71	6.607	11.3
1.0000	2.34	-	-	2.34	-	-	-	-

*These numbers refer to the number of the column, e.g., (2-5) means column (2) - column (5)

Figure 15

Figure 15

Kinetic Plots of Scavenging Mechanism

(Cyclohexane inhibition experiments)

$$\rho = \left\{ 1 + w \frac{(P)}{(C_6H_{12})} \right\} \frac{I}{d(H_2)/dt}$$

A: P = propylene

B: P = cyclohexene

C: P = benzene

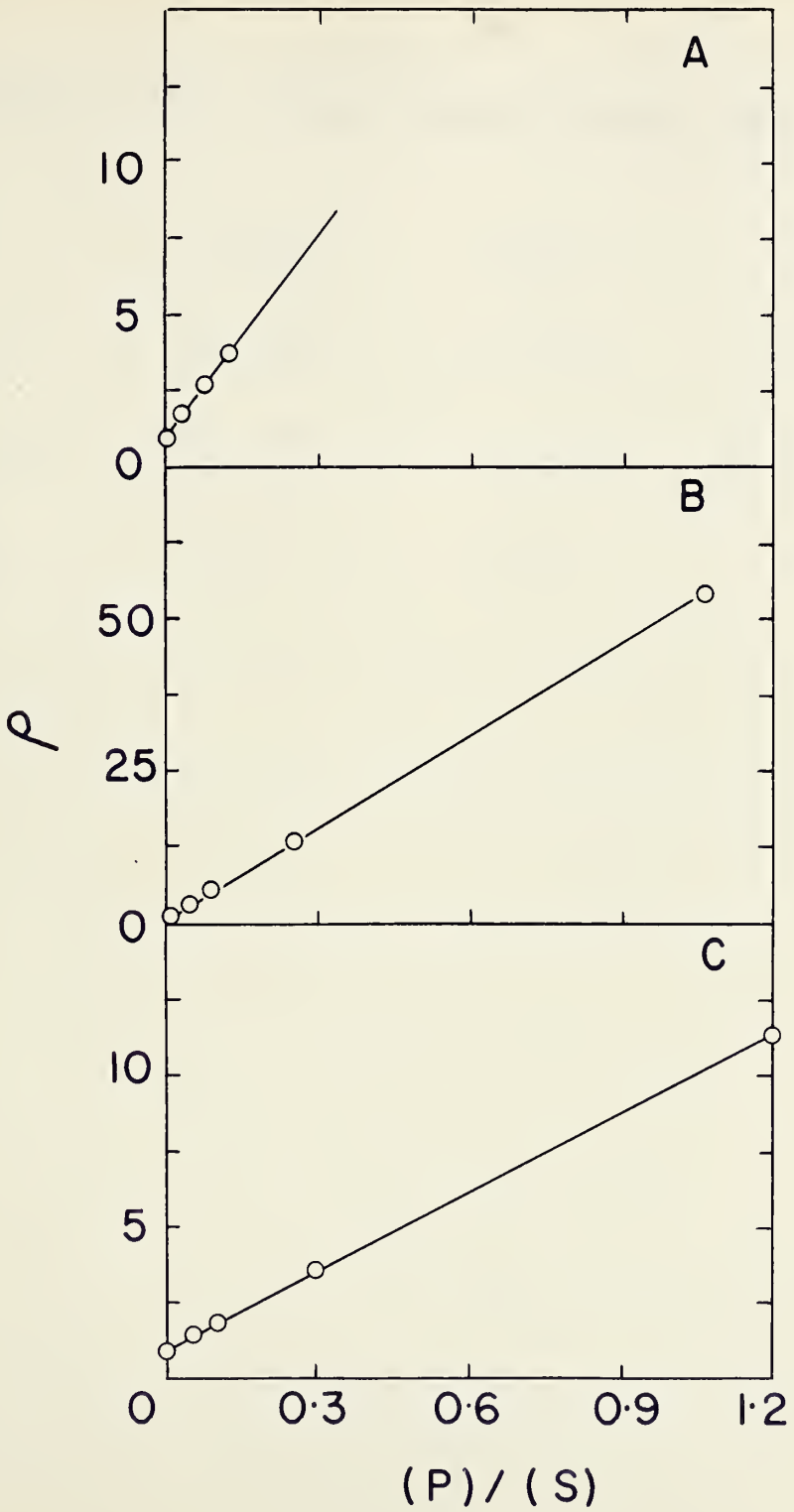

A
B
C
10
5
0
50
25
0
10
5
0
ρ
0
0·3
0·6
0·9
1·2
(P)/(S)

TABLE XXVII

Values of Rate Constant Ratios Obtained from Mechanism (1)

P	k_5/k_3	k_4/k_3	k_4/k_5
C_6H_6	2.5 ± 0.2	5.9 ± 0.5	2.4
c-C_6H_{10}	25 ± 10	31 ± 19	1.2
C_3H_6	>10	>105	11

values might not be unreasonable in the cases of cyclohexene and propylene if the hydrogen atoms are assumed to be epithermal. The value of k_5/k_3 obtained for benzene, however, is surprisingly high even for epithermal hydrogen atoms. It implies that abstraction of hydrogen from benzene is 2.5 times faster than from cyclohexane. The smaller amount of hydrogen in benzene and the stronger C-H bond in benzene than in cyclohexane make this seem unlikely. A possible complex mechanism may exist for reaction (5). With the data on hand, it is not possible to conceive the details of such a complex mechanism.

Now the energy transfer mechanism will be considered.

(2) Energy transfer mechanism

A general energy transfer mechanism which fits the experimental results can be written as follows:

$$C_6H_{12} \xrightarrow{I} C_6H_{12}^* \qquad \text{--(1)}$$

$$C_6H_{12}^* \longrightarrow H_2 + \text{products} \qquad \text{--(6)}$$

$$C_6H_{12}^* + P \longrightarrow C_6H_{12} + P^* \qquad \text{--(7)}$$

$$P^* \longrightarrow x\,H_2 + \text{products}, \quad 0 \leqslant x \leqslant 1 \qquad \text{--(8)}$$

The x signifies that perhaps not every P^* results in the formation of a hydrogen molecule. Reactions (6) and (8)

represent over-all processes and might comprise several steps each. Steady state treatment of this mechanism yields

$$\frac{d(H_2)}{dt} = k_6(C_6H_{12}^{*}) + x\, k_8(P^{*}) \qquad \text{--(xii)}$$

$$\frac{d(C_6H_{12}^{*})}{dt} = I - k_6(C_6H_{12}^{*}) - k_7(C_6H_{12}^{*})(P) = 0 \text{--(xiii)}$$

$$\frac{d(P^{*})}{dt} = k_7(C_6H_{12}^{*})(P) - k_8(P^{*}) = 0 \qquad \text{--(xiv)}$$

By rearranging equations (xiii) and (xiv) to obtain expressions for $(C_6H_{12}^{*})$ and (P^{*}) and substituting these expressions into equation (xii), equation (xv) can be obtained.

$$\frac{d(H_2)}{dt} = \frac{I\left(1 + x\,\frac{k_7}{k_6}(P)\right)}{1 + \frac{k_7}{k_6}(P)} \qquad \text{--(xv)}$$

Rearrangement of equation (xv) gives

$$\left[1 + y(P)\right]\; I/\frac{d(H_2)}{dt} = 1 + z(P) \qquad \text{--(xvi)}$$

$$= \rho'$$

where $y = x\, k_7/k_6$, $z = k_7/k_6$ and ρ' represents the left hand

side of equation (xvi).

Assuming arbitrary values for y, sets of values of ρ' were calculated. The calculated values of ρ' were plotted against the protector concentration, (P), in moles per litre (gas phase) in an attempt to obtain a straight line with an intercept of unity. Such a line was obtained for each system (see Tables XXVIII - XXX and Figure 16). The value of y that gave the desired line in each system, along with the slope of the line, z, and corresponding value of x, is presented in Table XXXI.

The value of the ratio of k_7/k_6 indicates the value of ratio of the rate of energy transfer to the rate of decomposition of the excited cyclohexane species. The value of the ratio k_7/k_6 in liquid cyclohexane - benzene was 0.78 litre per mole (58) and in liquid cyclohexane - cyclohexene was 0.54 litre per mole (61). Thus the value of this ratio in the gas phase is of the order of 10^3 times greater than in the liquid phase. This has three possible causes: (a) k_6 is much smaller in the gas than in the liquid phase; (b) K_7 is much larger in the gas than in the liquid; (c) both of (a) and (b).

The exact nature of $C_6H_{12}^*$ is not known, but it is most likely that it is either an electronically

TABLE XXVIII

Data for the Curve Fitting the Hydrogen Yield in Cyclohexane-Benzene Systems

Energy transfer mechanism y = 150 b = benzene c = cyclohexane

1 ϵ_b	2 $G(H_2)_{obs}$	3 b(moles/L) gas phase	4 $I = 8.1\epsilon_c$	5 $G(H_2)^{\circ}_b\epsilon_b$	6 (2-5)*	7 (4/6)* $= I/dH_2/dt$	8 $1+y(b)$	9 $f' = (7 \times 8)$*
0.0000	8.10	0.000	8.10	0.000	8.10	1.00	1.000	1.00
0.0085	7.91	0.149	8.03	0.013	7.90	1.02	1.022	1.04
0.0213	7.14	0.372	7.91	0.032	7.11	1.11	1.056	1.17
0.0424	5.88	0.744	7.76	0.064	5.82	1.33	1.112	1.48
0.0847	4.91	1.490	7.42	0.128	4.78	1.55	1.224	1.90
0.2102	3.52	3.720	6.41	0.318	3.20	2.00	1.560	3.12
0.5156	2.17	9.300	3.92	0.779	1.39	2.82	2.320	6.54
1.0000	1.51	-	-	1.510	-	-	-	-

* These numbers refer to the number of the column, e.g., (2-5) means column (2) - column (5)

TABLE XXIX

Data for the Curve Fitting the Hydrogen Yield in Cyclohexane-Cyclohexene Systems

Energy transfer mechanism y = 1200 o = cyclohexene c = cyclohexane

1 ϵ_o	2 $G(H_2)_{obs}$	3 o(moles/L) gas phase	4 $I = 8.1\epsilon_c$	5 $G(H_2)^\circ_o \epsilon_o$	6 (2-5)*	7 (4/6)* = $I/dH_2/dt$	8 $1 + y\ (o)$	9 $\rho' = (7 \times 8)$*
0.0000	8.10	0.000	8.10	0.000	8.10	1.00	1.000	1.00
0.0081	6.32	0.130	8.03	0.027	6.29	1.28	1.156	1.48
0.0204	5.31	0.330	7.93	0.069	5.24	1.51	1.396	2.11
0.0408	4.60	0.620	7.77	0.138	4.46	1.74	1.744	3.03
0.0816	4.52	1.300	7.44	0.276	4.24	1.75	2.560	4.50
0.2033	4.23	3.300	6.45	0.687	3.54	1.82	4.960	9.02
0.5053	3.53	8.140	4.01	1.708	1.82	2.20	10.768	23.7
1.0000	3.38	-	-	3.380	-	-	-	-

*These numbers refer to the number of the column, e.g., (2-5) means column (2) - column (5)

TABLE XXX

Data for the Curve Fitting the Hydrogen Yield in Cyclohexane-Propylene Systems

Energy transfer mechanism y = 1200 p = propylene c = cyclohexane

1 ϵ_p	2 $G(H_2)_{obs}$	3 p(moles/L) gas phase	4 $I = 8.1\epsilon_c$	5 $G(H_2)^{\circ}_p\epsilon_p$	6 (2-5)*	7 (4/6)* = $I/dH_2/dt$	8 $1 + y\ (p)$	9 $\rho' = (7 \times 8)$*
0.0000	8.10	0.000	8.10	0.000	8.10	1.00	1.000	1.00
0.0017	6.87	6.300	8.09	0.004	6.87	1.18	1.076	1.27
0.0136	5.70	48.01	7.99	0.032	5.67	1.41	1.576	2.22
0.0292	4.80	103.74	7.86	0.068	4.73	1.66	2.245	3.73
0.0592	4.32	207.23	7.62	0.139	4.18	1.82	3.475	6.32
0.2169	4.23	407.40	6.34	0.508	3.72	1.70	5.889	10.01
1.0000	2.34	856.80	-	2.340	-	-	-	-

*These numbers refer to the number of the column, e.g., (2-5) means column (2) - column (5)

Figure 16

Figure 16

Kinetic Plots of Energy Transfer Mechanism

(Cyclohexane inhibition experiments)

$$\rho' = \left[1 + y(P)\right] \; I / \frac{d(H_2)}{dt}$$

A: P = propylene

B: P = cyclohexene

C: P = benzene

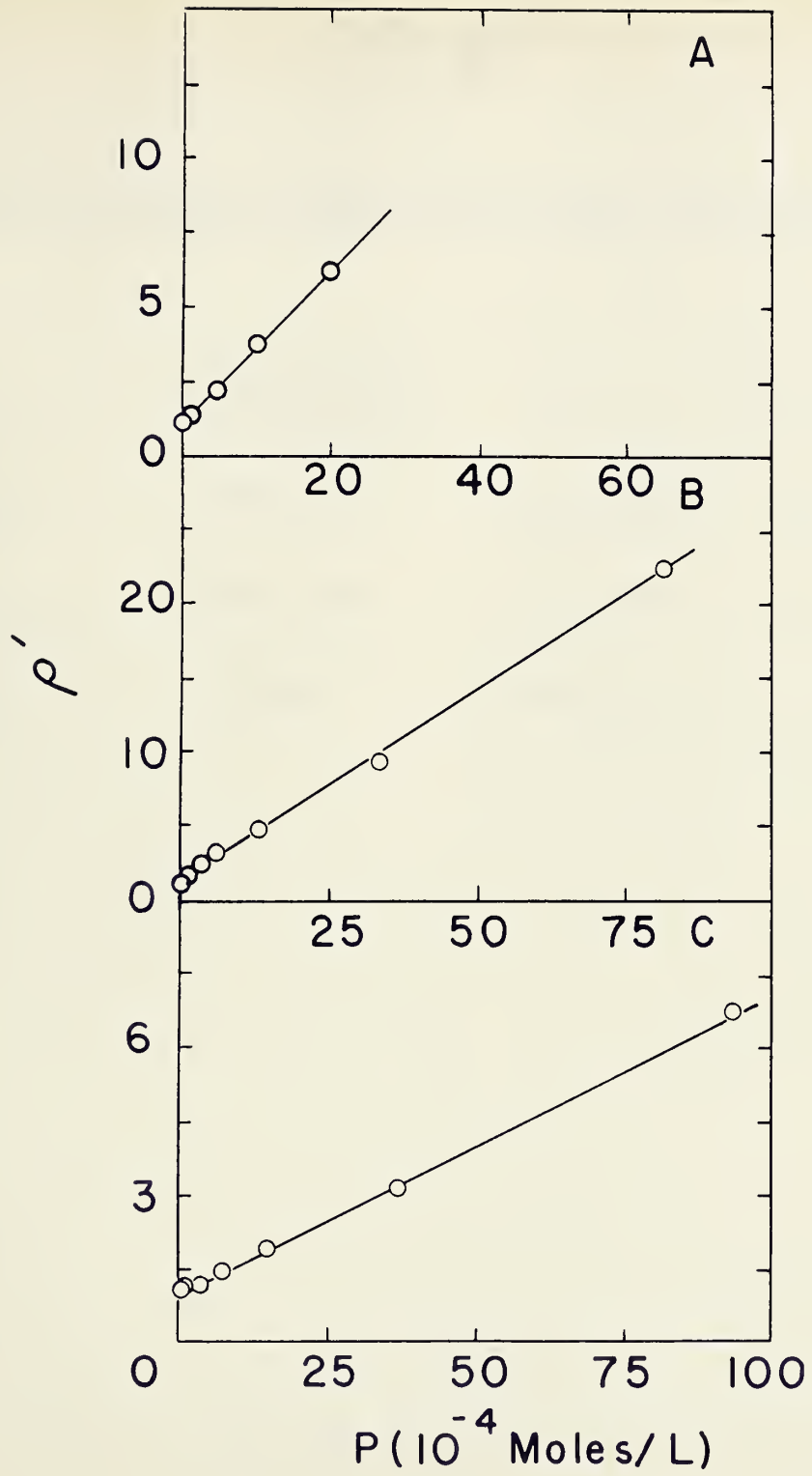

A
B
C
10
5
0
20
40
60
20
10
0
25
50
75
6
3
0
25
50
75
100
ρ'
P(10⁻⁴ Moles/L)

TABLE XXXI

Value of Kinetic Parameters Obtained from Mechanism (2)

P	y(litres/mole)	x	z(k_7/k_6, litre/mole)
C_6H_6	150 ± 18	0.25 ± 0.01	610 ± 25
C_6H_{10}	1200 ± 420	0.44 ± 0.01	2700 ± 800
C_3H_6	⩾ 1200	0.27 ± 0.01	⩾ 2570

excited molecule or a positive ion. Consider the above possible cause (a). If $C_6H_{12}^*$ were an electronically excited molecule, the rate of its decomposition might be the same in both the liquid and gaseous states. This would be especially true if the internal conversion of some of the electronic energy into vibrational energy occurs as rapidly as it is presently thought to occur (144). On the other hand, if $C_6H_{12}^*$ were a positive ion, and reaction (6) corresponds to the dissociative recombination of the ion and electron, k_6 would be several orders of magnitude smaller in the gas than in the liquid phase. It is believed that the lifetime of a positive ion in an irradiated liquid is of the order of 10^{-13} seconds (128). However, under the present conditions of gas phase irradiations, the lifetime of the positive ion has been calculated to be of the order of 10^{-3} seconds (see page 114 of this thesis). Thus k_6 might be smaller by a factor of the order of 10^{-10} in the gas phase than in the liquid phase.

Now consider the above possible cause (b), that k_7 is much larger in the gas than in the liquid. If reaction (7) occurred during physical molecular collisions, k_7 might be expected to be of the same order of magnitude in the two phases. Most theories of electronic excitation transfer imply that the value of k_7 in the gas phase would

be similar to or much smaller than the value in the liquid phase (e.g., the exciton theory (131), assuming that there is a certain degree of order in the liquid, and the sensitised fluorescence theory (24) imply much smaller rate constants in the gas phase). If $C_6H_{12}^*$ is the positive ion, it seems very likely that k_7 would be very much smaller in the gas phase than in the liquid phase (Ref. (132) combined with Ref. (129)).

In summary, if $C_6H_{12}^*$ were an electronically excited molecule, it appears that the value of the ratio k_7/k_6 in the gas phase should have been the same or smaller than in the liquid phase. If $C_6H_{12}^*$ were a positive ion, the value of the above ratio in the gas phase could easily be several orders of magnitude larger than in the liquid phase (about 10^{10} divided by the appropriate ratio of k_7 values in the two phases). The observed increase by a factor of about 10^3, when the phase is changed from liquid to gas, may be taken as an indication that $C_6H_{12}^*$ is a positive ion.

(B) Radiolyses of Benzene, Cyclohexene and Propylene

The data, for the radiolytic decomposition of benzene, cyclohexene and propylene are not extensive enough to draw any definite conclusions about the mechanisms of

decomposition. However, an attempt to postulate the formation of some of the products is made.

(a) Benzene

If the radiolytic decomposition of benzene is represented as

$$C_6H_6 \longrightarrow H_2 + X$$

then the total hydrogen deficiency in the yields of the products X should be equal to $G(H_2) = 1.38$. A material balance of the products obtained in the present work is given in Table XXXII.

It is clear from Table XXXII that the hydrogen equivalent of over one G unit of hydrocarbon products are missing. From the investigation of the alpha radiolysis of benzene by Mund and Bogaert (74), Burton (as in Ref.(74)) calculated G (polymer) $\simeq$ 4. Although this figure '4' may not be accurate, yet it is indicative of high polymerisation in the radiolysis of benzene vapour. If, in the present study, polymers with carbon numbers higher than 12 were formed, they would have remained undetected. Therefore this probably is the reason for poor agreement in the material balance.

According to molecular orbital theory, the electrons of each carbon atom in a benzene molecule exist in three coplanar sp^2 orbitals, making 120° angles with each other and

TABLE XXXII

G Values and Material Balance of Products from Irradiation of Benzene Vapour

The hydrogen equivalent of a product corresponds to the amount of hydrogen that was produced when that product was formed from benzene

Product	G(Products)	H_2 Equivalent
CH_4	0.13	- 0.20
C_2H_6	0.08	- 0.16
C_2H_4	0.07	- 0.07
C_2H_2	1.15	0.00
Total C_{12} hydrocarbons	0.31	0.00
	Total	- 0.43
H_2	1.38	1.38

in a p orbital normal to the plane of the sp^2 orbitals. These six p orbitals are pictured as interacting over the entire ring and not confined to any particular bond. These six π electrons form a charge cloud both above and below the plane of the carbon ring. These π electrons have free mobility in the molecular orbital formed by the interaction between p orbitals. This free mobility indicates that any energy or electrical influence on the ring is conveyed from one part of the molecule to another. Thus if the energy absorbed during irradiation is distributed over the entire molecule and thereby not confined to any particular bond, there might be insufficient accumulation of energy in any particular bond to cause it to rupture. This perhaps causes the relatively low yields observed in photochemical (133,134) and radiation chemical experiments (43,73,58).

(b) Cyclohexene

Cyclohexane has been reported as a major product in the radiolysis of cyclohexene in both the liquid (58) and vapour (73) phases. Benzene is also a product in the vapour phase (73). In the present work, besides cyclohexane and benzene, dicyclohexyl, cyclohexyl-cyclohexene, and dicyclohexenyl were found. Although cyclohexadiene might have been expected as a product, our analytical

system was inadequate for its detection.

If the decomposition of cyclohexene is considered as

$$c\text{-}C_6H_{10} \longrightarrow H_2 + X$$

then the total hydrogen deficiency in the yields of the products X should be equal to $G(H_2) = 3.1$. Table XXXIII gives a material balance of the products obtained in this study along with their G values.

It is evident from Table XXXIII that a deficiency of over 3 G units of hydrogen equivalents exists in the measured products. As was stated in the cases of cyclohexane and benzene, this deficiency might be ascribed to a polymer that was not measured in our analytical system. The formation of such polymers to the extent of 4 G units of cyclohexene was reported by Freeman (61) in the liquid phase radiolysis of cyclohexene.

It is not known to what relative extents free radical and ionic reactions are responsible for the observed products. Since very little is known about ion molecule reactions, it is virtually impossible to test their feasibility by kinetic calculations. A postulated free radical mechanism can be tested to a limited extent. The following partial mechanism is consistent with the observed product

TABLE XXXIII

Material Balance and G Values of Products Obtained in the Radiolysis of Cyclohexene Vapour

The hydrogen equivalent of a product corresponds to the amount of hydrogen that was produced when that product was formed from cyclohexene

Products	G(Products)	H_2 Equivalent
CH_4	0.28	- 0.28
C_2H_6	0.05	- 0.05
C_2H_4	1.55	0.00
C_2H_2	0.62	0.00
C_3H_6	0.07	0.00
C_3H_8	0.14	- 0.14
C_4 hydrocarbon (probably C_4H_6)	0.16	0.00
c-C_6H_{12}	1.35	- 1.35
C_6H_6	0.12	0.24
dicyclohexyl	0.16	- 0.16
cyclohexyl-cyclohexene	0.85	0.00
dicyclohexenyl	1.46	1.46
	Total	- 0.28
H_2	3.1	3.1

yields:

$$c\text{-}C_6H_{10} \xrightarrow{h\nu} c\text{-}C_6H_9 + H \qquad \text{--(1)}$$

$$H + c\text{-}C_6H_{10} \longrightarrow H_2 + c\text{-}C_6H_9 \qquad \text{--(2a)}$$

$$\longrightarrow c\text{-}C_6H_{11} \qquad \text{--(2b)}$$

$$c\text{-}C_6H_{11} + c\text{-}C_6H_{10} \longrightarrow c\text{-}C_6H_{12} + c\text{-}C_6H_9 \qquad \text{--(3)}$$

$$2\ c\text{-}C_6H_9 \longrightarrow c\text{-}(C_6H_9)_2 \qquad \text{--(4a)}$$

(dicyclohexenyl)

$$\longrightarrow c\text{-}C_6H_8 + c\text{-}C_6H_{10} \qquad \text{--(4b)}$$

$$c\text{-}C_6H_9 + c\text{-}C_6H_{11} \longrightarrow c\text{-}C_6H_9 - C_6H_{11} \qquad \text{--(5a)}$$

(cyclohexyl-cyclohexene)

$$\longrightarrow c\text{-}C_6H_8 + c\text{-}C_6H_{12} \qquad \text{--(5b)}$$

$$\longrightarrow 2\ c\text{-}C_6H_{10} \qquad \text{--(5c)}$$

$$2\ c\text{-}C_6H_{11} \longrightarrow (c\text{-}C_6H_{11})_2 \qquad \text{--(6a)}$$

(dicyclohexyl)

$$\longrightarrow c\text{-}C_6H_{10} + c\text{-}C_6H_{12} \qquad \text{--(6b)}$$

Assuming that free radicals are the only

precursors of the dimers, the value of the ratio $k_{5a} / (k_{4a}\, k_{6a})^{1/2}$ is given by

$$G(c\text{-}C_6H_9\text{-}C_6H_{11}) / \left[G(c\text{-}C_6H_9)_2\, G(c\text{-}C_6H_{11})_2\right]^{1/2} = 1.8$$

This is close to the statistically expected value of 2 (135). Similarly, assuming as a first approximation that reaction (3) in the major source of cyclohexane, it can be calculated that

$$k_3 / (k_{6a})^{1/2} \simeq 1.2\times10^{-3} \text{ (l/mole sec)}^{1/2}$$ (see footnote 1)

The gas phase rate constant k_{6a} will have a value of about 2×10^{10} l/mole sec. at 108°C (see footnote 2). Therefore $k_3 \simeq 2\times10^{2}$ l/mole sec. This value would be reduced by a factor of about three (i.e., to about 70 l/mole sec) if the amounts of cyclohexane generated in reactions (5b) and (6b) were considered.

The present value might be compared with the values

---

(1) This value was calculated using the dose rate (1.5×10^{12} ev/cc sec), the cyclohexene concentration (0.013M) and the yields of cyclohexane and dicyclohexyl.

(2) Assuming the collision diameter of cyclohexyl radicals is equal to that of cyclohexane, i.e., 6.5 Å (136) and that reaction (6a) has a steric factor of 0.1.

of the rate constants for hydrogen abstraction by other radicals from several hydrocarbons. These values of rate constants are presented in Table XXXIV.

From Table XXXIV, it is evident that there is a marked trend of decrease in the values of rate constants, from hydrogen through methyl to ethyl radicals. Although the values in Table XXXIV are very crude, the large decrease in the rate constant from the ethyl to the cyclohexyl radical in the abstraction of hydrogen from cyclohexene is consistent with the trend.

Although some of the hydrogen and $c\text{-}C_6H_9$ radicals might have been formed by the reactions

$$c\text{-}C_6H_{10} \longrightarrow c\text{-}C_6H_{10}^{+} + e \qquad \text{--(7)}$$

$$c\text{-}C_6H_{10}^{+} + c\text{-}C_6H_{10} \longrightarrow c\text{-}C_6H_{11}^{+} + c\text{-}C_6H_9 \qquad \text{--(8)}$$

$$c\text{-}C_6H_{11}^{+} + e \longrightarrow c\text{-}C_6H_9 + H_2 \qquad \text{--(9)}$$

it is unlikely that any of the $c\text{-}C_6H_{11}$ radicals were formed by

$$c\text{-}C_6H_{11}^{+} + e \longrightarrow c\text{-}C_6H_{11} \qquad \text{--(10)}$$

because the free radicals thus produced would possess too much energy to be stable. The most reasonable source of $c\text{-}C_6H_{11}$ radicals seems to be reaction (2b). For similar

TABLE XXXIV

Rate Constants at 108°C for Hydrogen Abstraction Calculated from the Kinetic Parameters in References Cited

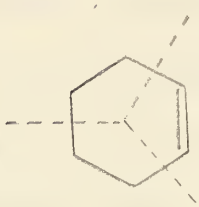
$R + R'H \longrightarrow RH + R'$

R	R H	k(l/mole sec)	Reference
$c\text{-}C_6H_{11}$	$c\text{-}C_6H_{10}$	70	present work
C_2H_5	$c\text{-}C_6H_{10}$	5500	(137)
C_2H_5	$n\text{-}C_7H_{16}$	430	(138)
CH_3	$n\text{-}C_6H_{14}$	2960	(138)
CH_3	$c\text{-}C_6H_{12}$	3400	(138)
H	$n\text{-}C_6H_{14}$	55000	(138)
H	$c\text{-}C_6H_{12}$	220000	(138)

reasons, reaction (3) seems to be a reasonable source of cyclohexane.

The formation of lower hydrocarbons indicates that two types of ring fission occur, if the C_4 olefin is butadiene.

I $\longrightarrow C_2H_4 + C_4H_6$

II  $\longrightarrow 2\ C_2H_4 + C_2H_2$

The approximate G values of cyclohexene undergoing fission of types I and II are 0.16 and 0.7 respectively. Thus $G(C_4) + 2\ G(C_2H_2) = 1.42$ agrees reasonably well with $G(C_2H_4) = 1.57$.

(c) Propylene

Experimental difficulties prevented the determination of the yields of products other than hydrogen and methane. A value of $G(H_2) = 2.21$ obtained in the present work can be compared with $G(H_2) = 1.3 - 2.4$ calculated for propylene from Back's (79,80) results and with $G(H_2) = 1.5$ obtained by Kang Yang (139). With the limited data, no definite conclusions could be drawn regarding the mechanism of its decomposition.

(C) Methyl Cyclohexane and its Binary Solutions

(a) Pure methyl cyclohexane

From the radiolysis of methyl cyclohexane as a function of dose, only a few general conclusions could be drawn. Since no measurable amounts of liquid products were obtained, a material balance could not be worked out. On the basis of the experimental work done in connection with cyclohexane and ethanol (discussion later), one might have expected C_7 and C_{14} hydrocarbon products to be formed. It is not clear why methyl cyclohexane gave no measurable liquid products. This might be an indication that the polymerisation reaction, previously noted in the cyclohexane system was more extensive in the methyl cyclohexane system. The observations are far too few to propose a mechanism for its radiolytic decomposition, except the usual formation of excited and ionised molecules followed by the rupture of these species. The yield of gases volatile at -196°C appears to be independent of dose (see Figure 10). The average G value of gases non-condensable at -196°C is about 6.1 ± 0.2. The decrease in the G values of gases volatile at -112°C in the low dose region may not be real (see Figure 10). The amounts of gases volatile at -112°C were so small that they could not be accurately measured. This might be the cause

for the sharp decrease in the yields of gases volatile at -112°C in the low dose region. However, in the dose range 2×10^{19} ev to 17×10^{19} ev, the G value is approximately constant at 0.9.

(b) Inhibition experiments

The curves obtained for the inhibition studies of methyl cyclohexane were not smooth (see Figure 11). A general decrease in the yields of gases volatile at -196°C was, however, observed with increasing concentration of the inhibitor in each case. The experimental results of the inhibition runs of methyl cyclohexane are not precise enough to serve as a test of a particular mechanism. They may, however, be treated according to the two mechanisms obtained for the cyclohexane system to obtain crude values for the kinetic parameters of those mechanisms.

(1) Scavenging mechanism

$$C_7H_{14} \rightsquigarrow C_7H_{14}^{*} \qquad \text{--(1)}$$

$$C_7H_{14}^{*} \longrightarrow H + C_7H_{13} \qquad \text{--(2)}$$

$$H + C_7H_{14} \longrightarrow H_2 + C_7H_{13} \qquad \text{--(3)}$$

$$H + P \longrightarrow PH \qquad \text{--(4)}$$

$$H + P \longrightarrow H_2 + P\text{-} \qquad \text{--(5)}$$

In the above equations, C_7H_{14} represents methyl cyclohexane, P represents the protector, PH and P the corresponding radicals. By analogy with the cyclohexane systems, steady state treatment of this mechanism yields

$$\left\{1 + w \frac{(P)}{(C_7H_{14})}\right\} \frac{I}{d(H_2)/dt} = 1 + v \left\{\frac{(P)}{(C_7H_{14})}\right\} = \rho$$

where $w = k_5/k_3$, $v = (k_4 + k_5)/k_3$ and ρ represents the left hand side of the equation.

The numerical values of $I / \frac{d(H_2)}{dt}$ were determined from the experimental data.

By giving arbitrary values to w, sets of values of ρ were calculated. These sets of values were plotted against the ratio $(P) / (C_7H_{14})$ to see if a straight line could be obtained.

The value of ρ which best fits the experimental data and the corresponding values of $I / \frac{d(H_2)}{dt}$ are presented in Tables XXXV and XXXVI. The lines obtained are shown in Figure 17. The values of the various ratios of rate constants are summarised in Table XXXVII.

(2) Energy (ionisation or excitation) transfer mechanism

TABLE XXXV

Data for the Curve Fitting the (-196°C) Fraction Yield in Methyl Cyclohexane-Benzene Systems

Scavenging mechanism w = 3 b = benzene mc = methyl cyclohexane

1 ϵ_b	2 $G(H_2)_{obs}$**	3 (b)/(mc)	4 $I = 6.3\epsilon_{mc}$	5 $G(H_2)^{\circ}_b \epsilon_b$	6 (2-5)*	7 (4/6)* = $I/dH_2/dt$	8 $1 + w\ \frac{(b)}{(mc)}$	9 $\rho = (7 \times 8)$*
0.0000	6.30	0.0000	6.30	0.000	6.30	1.00	1.000	1.00
0.0108	5.80	0.0145	6.23	0.016	5.78	1.08	1.044	1.13
0.0215	5.50	0.0293	6.16	0.032	5.47	1.12	1.088	1.22
0.0430	5.80	0.0598	6.03	0.065	5.73	1.05	1.179	1.24
0.0857	5.30	0.1248	5.76	0.129	5.17	1.11	1.375	1.53
0.2123	4.50	0.3592	4.96	0.319	4.18	1.19	2.078	2.47
0.4181	2.60	0.9884	3.67	0.627	1.97	1.86	3.965	7.37
1.0000	1.51	-	-	1.510	-	-	-	-

* These numbers refer to the number of the column, e.g., (2-5) means column (2) - column (5)

** G(-196°C) is taken as a measure of $G(H_2)$. The numbers in column 2 are really the yields of gases volatile at -196°C

TABLE XXXVI

Data for the Curve Fitting the (-196°C) Fraction Yield in Methyl Cyclohexane-Cyclohexene Systems

Scavenging mechanism w = 5 o = cyclohexene mc = methyl cyclohexane

1 ϵ_o	2 $G(H_2)^{**}_{obs}$	3 (o)/(mc)	4 $I = 6.3\epsilon_{mc}$	5 $G(H_2)^{\circ}_{o}\epsilon_o$	6 (2-5)*	7 (4/6)* = I/ dH_2/dt	8 $1 + w\frac{(o)}{(mc)}$	9 $\rho = (7 \times 8)^*$
0.0000	6.30	0.0000	6.30	0.000	6.30	1.00	1.000	1.00
0.0103	5.12	0.0127	6.24	0.035	5.09	1.23	1.064	1.31
0.0206	4.33	0.0257	6.17	0.070	4.26	1.45	1.129	1.64
0.0431	4.43	0.0525	6.03	0.146	4.28	1.41	1.263	1.78
0.0900	3.84	0.1095	5.73	0.304	3.54	1.62	1.548	2.51
0.2055	3.64	0.3149	5.01	0.695	2.95	1.70	2.575	4.38
0.4081	2.95	0.8731	3.73	1.379	1.57	2.38	5.366	12.75
1.0000	3.38	-	-	3.380	-	-	-	-

*These numbers refer to the number of the column, e.g., (2-5) means column (2) - column (5)

**G(-196°C) is taken as a measure of $G(H_2)$. The numbers in column 2 are really the yields of gases volatile at -196°C

Figure 17

Figure 17

Kinetic Plots of Scavenging Mechanism

(Methyl Cyclohexane inhibition experiments)

$$\rho = \left\{1 + w \frac{(P)}{(mc)}\right\} \frac{I}{d(H_2)/dt}$$

A: P = cyclohexene

B: P = benzene

mc = methyl cyclohexane

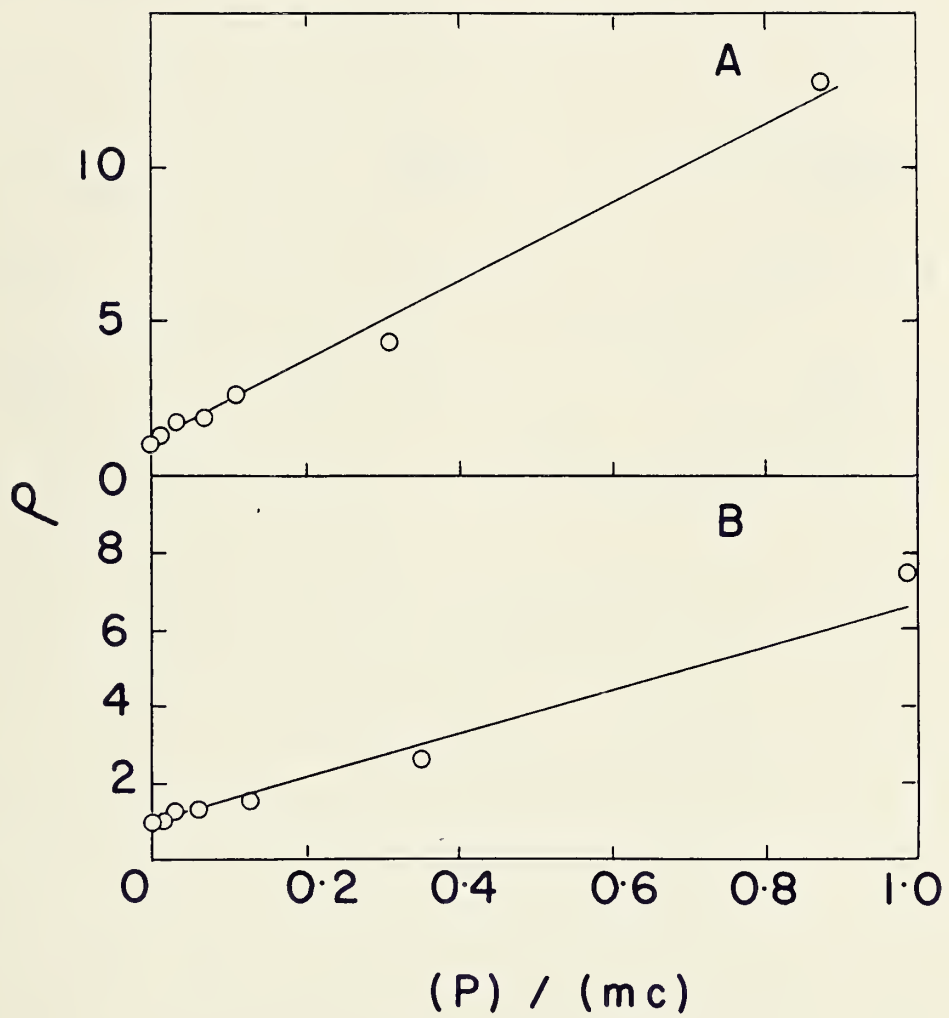

A
B
10
5
0
8
6
4
2
0
0·2
0·4
0·6
0·8
1·0
ρ
(P) / (mc)

TABLE XXXVII

Values of Rate Constant Ratios Obtained from Scavenging Mechanism

P	k_5/k_3	k_4/k_3
C_6H_6	3 ± 3	2.6 ± 0.2
$c\text{-}C_6H_{10}$	> 5	> 9

$$C_7H_{14} \xrightarrow{I} C_7H_{14}^{*} \qquad \text{--(1)}$$

$$C_7H_{14}^{*} \longrightarrow H_2 + \text{products} \qquad \text{--(6)}$$

$$P + C_7H_{14}^{*} \longrightarrow P + C_7H_{14} \qquad \text{--(7)}$$

$$P^{*} \longrightarrow x\ H_2 + \text{products},\ 0 \leq x \leq 1 \qquad \text{--(8)}$$

The x signifies that perhaps not every P^{*} results in the formation of a hydrogen molecule. Reactions (6) and (8) represent over-all processes and might comprise several steps each. By analogy with the cyclohexane system, steady state treatment of this mechanism gives

$$\left[1 + y\,(P)\right]\left[I/\ d(H_2)/dt\right] = 1 + z\,(P) = \rho'$$

where $y = x\ k_7/k_6$, $z = k_7/k_6$ and ρ' represents the left hand side of the above equation.

Assuming arbitrary values for y, sets of values of ρ' were calculated and plotted against the protector concentration, (P) in an attempt to obtain a straight line with an intercept of unity. The lines that best fit the experimental data are shown in Figure 18 (see also Tables XXXVIII and XXXIX). The value of y, along with the slope of the line, z, and corresponding value of x, is presented for each system in Table XL.

TABLE XXXVIII

Data for the Curve Fitting the (-196°C) Fraction Yield in Methyl Cyclohexane-Benzene Systems

Energy transfer mechanism y = 600 b = benzene mc = methyl cyclohexane

1 ϵ_b	2 $G(H_2)^{**}_{obs}$	3 b(moles/L) gas phase	4 $I = 6.3\epsilon_{mc}$	5 $G(H_2)^{\circ}_b\epsilon_b$	6 (2-5)*	7 (4/6)* = $I/dH_2/dt$	8 $1 + y\,(b)$	9 $\rho' = (7 \times 8)$*
0.0000	6.30	0.000	6.30	0.000	6.30	1.00	1.000	1.00
0.0108	5.80	0.186	6.23	0.016	5.78	1.08	1.111	1.20
0.0215	5.50	0.372	6.16	0.032	5.47	1.12	1.223	1.37
0.0430	5.80	0.743	6.03	0.065	5.73	1.05	1.446	1.52
0.0857	5.30	1.486	5.76	0.129	5.17	1.11	1.892	2.10
0.2123	4.50	3.715	4.96	0.319	4.18	1.19	3.230	3.84
0.4181	2.60	7.430	3.67	0.627	1.97	1.86	5.460	10.16
1.0000	1.51	-	-	1.510	-	-	-	-

*These numbers refer to the number of the column, e.g., (2-5) means column (2) - column (5)

**G(-196°C) is taken as a measure of $G(H_2)$. The numbers in column 2 are really the yields of gases volatile at -196°C

TABLE XXXIX

Data for the Curve Fitting the (-196°C) Fraction Yield in Methyl Cyclohexane-Cyclohexene Systems

Energy transfer mechanism y = 600 o = cyclohexene mc = methyl cyclohexane

1 ϵ_o	2 $G(H_2)^{**}_{obs}$	3 o(moles/L) gas phase	4 $I = 6.3\epsilon_{mc}$	5 $G(H_2)^{\circ}_{o}\epsilon_o$	6 (2-5)*	7 (4/6)* = $I/dH_2/dt$	8 1+y (o)	9 $\rho' = (7 \times 8)^*$
0.0000	6.30	0.000	6.30	0.000	6.30	1.00	1.000	1.00
0.0103	5.12	0.163	6.24	0.035	5.09	1.23	1.098	1.35
0.0206	4.33	0.326	6.17	0.070	4.26	1.45	1.196	1.73
0.0431	4.43	0.651	6.03	0.146	4.28	1.41	1.391	1.96
0.0900	3.84	1.303	5.73	0.304	3.54	1.62	1.782	2.89
0.2055	3.64	3.257	5.01	0.695	2.95	1.70	2.954	5.02
0.4081	2.95	6.514	3.73	1.379	1.57	2.38	4.910	11.67
1.0000	3.38	-	-	3.380	-	-	-	-

* These numbers refer to the number of the column, e.g., (2-5) means column (2) - column (5)

** G(-196°C) is taken as a measure of $G(H_2)$. The numbers in column 2 are really the yields of gases volatile at -196°C

Figure 18

Figure 18

Kinetic Plots of Energy Transfer Mechanism

(Methyl cyclohexane inhibition experiments)

$$\rho' = [1 + y(P)] \; [I / d(H_2)/dt]$$

A: P = cyclohexene

B: P = benzene

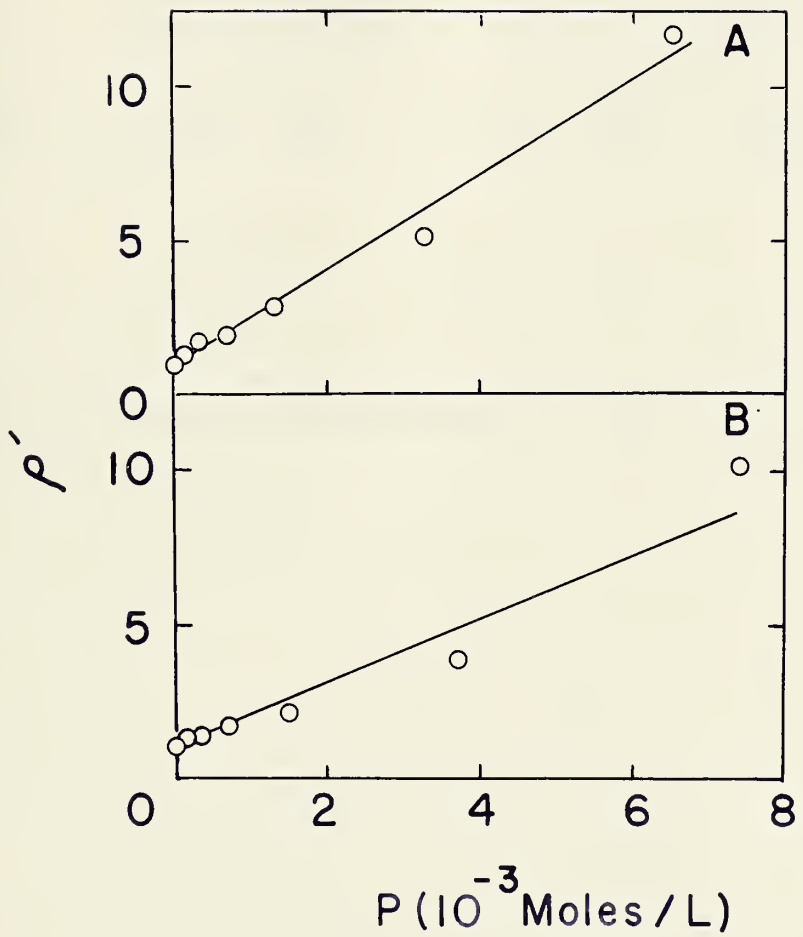

A
B
10
5
0
10
5
0
2
4
6
8
ρ'
P (10^-3 Moles / L)

TABLE XL

Values of Kinetic Parameters Obtained from Energy Transfer Mechanism

P	y(litres/mole)	x	z(k_7/k_6, litres/mole)
C_6H_6	600 ± 540	0.5 ± 0.2	1000 ± 800
$c\text{-}C_6H_{10}$	≈ 600*	≈ 0.4 ± 0.1	≈ 1500*

* within a factor of 2.

Comments on the values of the ratios of rate constants will be reserved until the end of the thesis.

(D) Ethanol and its Binary Solutions

(a) Pure ethanol

Previous studies on the radiolysis of liquid ethanol have shown that hydrogen is the major single product (85,88). The values of $G(H_2)$ obtained in these investigations are around 4.0. The vapour phase radiolysis of ethanol has yielded in the present work an average $G(H_2)$ value of 8.9 (see Table XIX). The higher $G(H_2)$ value obtained in the vapour phase radiolysis of ethanol is compatible with the idea that gas phase yields should be higher than the liquid phase yields (see Page 110 of this thesis).

If the decomposition of ethanol vapour is represented as

$$C_2H_5OH \longrightarrow H_2 + X$$

then the total hydrogen deficiency in the initial yields of the products X should be equal to $G(H_2)_i$. Since the yields of some of the products decreased with dose and since G_i could not be satisfactorily obtained for them, a material balance was worked out by using the G values of products obtained at 12.7×10^{20} ev dose (see Table XX).

In order to obtain a material balance, the following stoichiometric equations were assumed for the formation of various products.

$$n\ C_2H_5OH = H_2 + CH_3CHO$$

$$= H_2 + CH_4 + CO$$

$$= H_2 + (CH_3CHOH)_2$$

$$= H_2 + C_2H_2 + H_2O$$

$$= C_2H_4 + H_2O$$

$$= C_4H_9OH + H_2O$$

$$= C_3H_7OH + H_2 + CH_2O$$

$$= CH_4 + CH_2O$$

$$= CH_4 + CH_3CHOHCH_2OH$$

$$= C_2H_6 + CH_3CHO + H_2O$$

$$= CH_4 + CH_3OH + CH_3CHO$$

From the above equations, the formation of hydrogen, water and methane could be correlated to the formation of other products.

$$G(H_2) = G(CH_3CHOH)_2 + G(CO) + G(CH_3CHO\text{-}C_2H_6) + G(C_3H_7OH)$$

$$+ G(C_2H_2) \quad - G(CH_3OH)$$

Using the G values of products on the right hand side of this equation from Table XX, $G(H_2) = 7.2 - G(CH_3OH)$. Similarly

$$G(H_2O) = G(C_2H_4) + G(C_2H_2) + G(C_4H_9OH) + G(C_2H_6)$$

$$= 1.2 \quad \text{(from Table XX)}$$

$$G(CH_4) = G(CO) + G(CH_2O) - G(C_3H_7OH) + G(CH_3CHOHCH_2OH)$$

$$+ G(CH_3OH) = 1.55 + G(CH_3OH) \quad \text{(from Table XX)}$$

The value of $G(H_2) = 7.2 - G(CH_3OH)$ and $G(CH_4) = 1.55 + G(CH_3OH)$ are in approximate agreement with the observed values, $G(H_2) = 7.6$ and $G(CH_4) = 1.7$ if $G(CH_3OH)$ is small. From the above, an approximate expected yield of methanol would be $\left[G(CH_4)_{obs} - 1.55\right] = 0.1$. In the liquid phase radiolysis of ethanol (85), the value of the ratio of yields of formaldehyde to methanol is 0.2. If this ratio has the same value in the vapour phase, the expected yield of methanol would be about 0.2. Thus the methanol yield is probably quite small, although methanol could not be measured by the present analytical system.

The predicted value of $G(H_2O) = 1.2$ is much lower

than the observed value of 5.4. Three consecutive experiments yielded a G value of 5.4 ± 0.5 for water. The source of this excess water is not obvious. It might have been formed by reactions not considered in the following mechanism or the sample might have absorbed water from the atmosphere during the analytical procedure. An unaccountable excess of water was also observed by Mc Donell and Newton (85) in liquid phase radiolysis of ethanol.

A mass balance for carbon, hydrogen and oxygen has been worked out for various products and is presented in Table XLI. This mass balance corresponds to an empirical formula $C_{2.00}\ H_{6.76}\ O_{1.36}$ which has slightly more hydrogen and oxygen in it than ethanol.

To facilitate the discussion of the mass balance, a mechanism for the radiolytic decomposition of ethanol vapour is proposed as follows (see Pages 167 and 168 of this thesis). This mechanism explains the formation of the various products obtained by decomposition of both excited and ionised ethanol molecules.

If water is generated only by reactions (8c) and (14a), then $G(H_2O)$ should be equal to 1.2 (see earlier). The excess water in G units is (5.4 - 1.2)= 4.2. If the corresponding amounts of H (8.4) and O (4.2) are subtracted from the mass balance in Table XLI, the empirical formula becomes $C_{2.00}\ H_{6.02}\ O_{0.99}$.

TABLE XLI

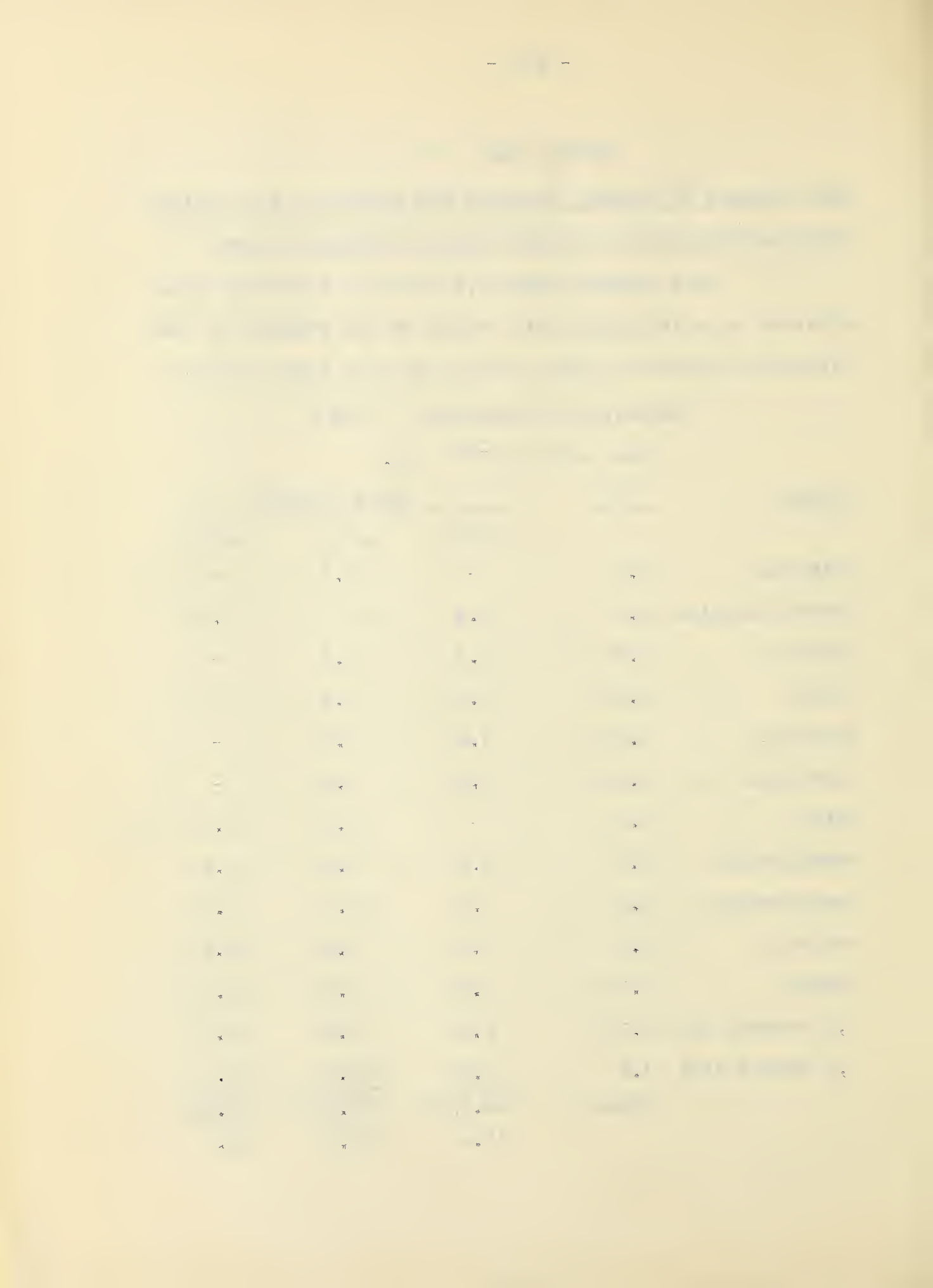
Mass Balance of Carbon, Hydrogen and Oxygen in the Various Products Obtained in the Radiolysis of Ethanol Vapour

The numbers under C,H and O in the table were obtained by multiplying the G value of the product by the respective number of atoms of C,H or O in that product

Irradiation temperature = 108°C

Dose (ev) x 10^{-20} = 12.7

Product	G	Mass balance		
		C	H	O
Hydrogen	7.6	-	15.2	-
Carbon monoxide	1.1	1.1	-	1.1
Methane	1.66	1.7	6.6	-
Ethane	0.23	0.5	1.4	-
Ethylene	0.72	1.4	2.9	-
Acetylene	0.03	0.1	0.1	-
Water	5.4	-	10.8	5.4
Formaldehyde	0.9	0.9	1.8	0.9
Acetaldehyde	4.5	9.0	18.0	4.5
Propanol	0.6	1.8	4.8	0.6
Butanol	0.19	0.8	1.9	0.2
1,2 Propane diol	0.15	0.5	1.2	0.3
2,3 Butane diol	1.2	4.8	12.0	2.4
	Total	22.7/2	76.7/6	15.4/1
		11.4	12.8	15.4



$$CH_3CH_2OH \longrightarrow CH_3CH_2OH^{*} \quad \text{--(1a)}$$

$$\longrightarrow CH_3CH_2OH^{+} + e \quad \text{--(1b)}$$

$$CH_3CH_2OH \longrightarrow CH_3CHOH + H \quad \text{--(2a)}$$

$$\longrightarrow CH_3 + CH_2OH \quad \text{--(2b)}$$

$$H + CH_3CH_2OH \longrightarrow H_2 + CH_3CHOH \quad \text{--(3)}$$

$$CH_3 + CH_3CH_2OH \longrightarrow CH_4 + CH_3CHOH \quad \text{--(4)}$$

$$CH_3 + CH_3CHOH \longrightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix} \!\!> CHOH \quad \text{--(5a)}$$

$$\longrightarrow CH_4 + CH_3CHO \quad \text{--(5b)}$$

$$CH_3CHOH + CH_2OH \longrightarrow CH_3CH(OH)CHOH \quad \text{--(6a)}$$

$$\longrightarrow CH_3CH_2OH + CH_2O \quad \text{--(6b)}$$

$$\longrightarrow CH_3CHO + CH_3OH \quad \text{--(6c)}$$

$$2\ CH_3CHOH \longrightarrow CH_3CHOHCHOHCH_3 \quad \text{--(7a)}$$

$$\longrightarrow CH_3CH_2OH + CH_3CHO \quad \text{--(7b)}$$

$$CH_3CH_2OH \longrightarrow CH_3CHO + H_2 \quad \text{--(8a)}$$

$$\longrightarrow CH_2O + CH_4 \quad \text{--(8b)}$$

$$\longrightarrow C_2H_4 + H_2O \quad \text{--(8c)}$$

$$C_2H_4 + H \longrightarrow C_2H_5 \qquad \text{--(9)}$$

$$2\ C_2H_5 \longrightarrow C_4H_{10} \qquad \text{--(10a)}$$

$$\longrightarrow C_2H_4 + C_2H_6 \qquad \text{--(10b)}$$

$$C_2H_5 + CH_3CH_2OH \longrightarrow C_2H_6 + CH_3CHOH \qquad \text{--(11)}$$

$$C_2H_5 + CH_3CHOH \longrightarrow \begin{matrix} CH_3 \\ C_2H_5 \end{matrix} \!\!> CHOH \qquad \text{--(12a)}$$

$$\longrightarrow C_2H_6 + CH_3CHO \qquad \text{--(12b)}$$

$$\longrightarrow C_2H_4 + C_2H_5OH \qquad \text{--(12c)}$$

$$CH_3CH_2OH + CH_3CH_2OH \longrightarrow CH_3CH_2OH_2 + C_2H_5O \qquad \text{--(13)}$$

where C_2H_5O represents the 3 position isomers and not just the ethoxy radical

$$CH_3CH_2OH_2 \longrightarrow CH_3CH_2 + H_2O \qquad \text{--(14a)}$$

$$\longrightarrow CH_3CH_2O + H_2 \qquad \text{--(14b)}$$

$$CH_3CHOH + CH_3CH_2O \longrightarrow CH_3CHO + C_2H_5OH \qquad \text{--(15a)}$$

$$\longrightarrow CH_3\underset{\displaystyle O\text{-}C_2H_5}{\overset{\displaystyle |}{CH}}\text{-}OH \qquad \text{--(15b)}$$

$$\downarrow$$

$$CH_3CHO + CH_3CH_2OH \qquad \text{--(15c)}$$

This good mass balance indicates that little or no polymer is formed during irradiation of ethanol. The calibration curve (similar to that on page 70 of this thesis) obtained during the ethanol experiments showed no decrease in source intensity. In the radiolysis of hydrocarbons, there was a poor mass balance and a decrease in source intensity due to the deposition of polymer on the surface of the source. The lack of decrease in source intensity and a good mass balance in the ethanol irradiations corroborate little or no polymer formation during its radiolysis.

Formation of products in the radiolysis of ethanol vapour.

Hydrogen:

McDonell and Newton (85) and Burr (88) have postulated that H atoms are formed by splitting off from the CH_2 group during the radiolysis of liquid ethanol. Burr, from his experimental evidence, states that to a large extent, the H atom then abstracts hydrogen from the OH group, and to a minor extent from the CH_3 group. Consider, however, the bond dissociation energies in ethanol. The dissociation energies of the primary C-H bonds and the secondary C-H bonds are about 96 K. cals/mole and 85 - 90 K. cals/mole respectively (141). The C - C bond dissociation energy is about 80 K. cals/mole and that of the C - O bond is about 90 K. cals/mole (141). The bond dissociation energy of O - H in ethanol is about

102 K. cals/mole (142). Thus the weakest —H bonds in ethanol are in the $-CH_2-$ group and the strongest is in the -OH group. It would therefore be surprising if H atom abstraction occurred largely at the -OH group and not at all at the $-CH_2-$ group. At present, no definite conclusions can be drawn.

Acetaldehyde:

Acetaldehyde may be formed by reactions (5b), (6c), (7b), (8a), (12 b) and (15). The radicals involved in these reactions are CH_3, C_2H_5, CH_3CH_2O, CH_3CHOH and CH_2OH. From the G values of products which require these radicals for their formation, the amounts of CH_3, C_2H_5, (CH_3CHOH CH_3CH_2O) and CH_2OH radicals can be calculated to be respectively 1.1 to 2.3 (depending on the mechanism for formation of CO), 0.43, 12 .35 and 1.05 G units. Since the concentration of CH_3CHOH radicals is much greater than that of any other radical, the disproportionation reaction of CH_3CHOH radicals (reaction 7b) might be considered as a major source of acetaldehyde. In reaction (15b), the hemi-acetal formed is known to be very unstable (140) and even if formed will decompose to acetaldehyde and ethanol.

Methane and Formaldehyde

Since the C-C bond is the weakest in the ethanol molecule, one might have expected a large yield of products

resulting from CH_3 and CH_2OH radicals in the gas phase. In the liquid phase, there may be recombination of the CH_3 and CH_2OH radicals in the Franck - Rabinowitch cages and hence the yields of the corresponding products would be low. Low yields of methane and formaldehyde were experimentally observed by McDonell and Newton (85). In the gas phase, where the cage effect will not be operative, larger yields of methane and formaldehyde were observed in the present work.

To a large extent methane is formed by abstraction reaction (4). Formaldehyde may arise from reactions (6b) and (8b). From the existing data the relative contribution of these reactions towards formaldehyde formation is not known.

Other products

The high yield of water was questioned earlier in the thesis and no explanation can be offered at present.

Carbon monoxide might be formed by the decomposition of formaldehyde or acetaldehyde.

Propanol and butanol are formed by the addition of methyl and ethyl radicals to CH_3CHOH radicals.

The vicinal glycols (2,3 butane diol and 1,2 propane diol) that were measured in the present investigation,

were probably formed by combination of CH_3CHOH radicals with themselves and with CH_2OH radicals. If CH_2CH_2OH radicals were present in appreciable concentration during the decomposition of ethanol, the combination of CH_2CH_2OH radicals with each other and with CH_3CHOH would have led to the formation of 1,4 butane diol and 1,3 butane diol. Since these products were not produced to a measurable extent, the concentration of CH_2CH_2OH radicals was negligible in the present system.

The ethyl radicals produced by reactions (9) and (14a) might abstract or disproportionate to give ethane. Since the value of the ratio of disproportionation to combination of ethyl radicals is about 0.12 (143), the amount of ethane from reaction (10b) would be about one eighth of the amount of butane. The yield of butane in the present work was only a trace and thus a negligible amount of ethane originates from the disproportionation reaction. Therefore the major source of ethane is probably reaction (11).

Ethylene, which has an appreciable yield, is assumed to be formed by reactions (8c), (10b) and (12c). Since reaction (10b) was precluded as a major source of ethane, not much ethylene is produced by reaction (10b) either.

(b) Inhibition experiments

The experimental data were tested against the two

reaction mechanisms that gave straight line plots for the vapour solutions of cyclohexane with benzene cyclohexene or propylene. The two mechanisms will be treated separately, making the simplifying assumption that the variation of the total gas fraction volatile at -196°C is a measure of the variation of the hydrogen yield.

(1) Scavenging mechanism

$$C_2H_5OH \xrightarrow{I} C_2H_5OH^* \qquad --(1)$$

$$C_2H_5OH^* \longrightarrow H + C_2H_5O \text{ or } C_2H_4OH \qquad --(2)$$

$$H + C_2H_5OH \longrightarrow H_2 + C_2H_4OH \qquad --(3)$$

$$H + P \longrightarrow PH \qquad --(4)$$

$$H + P \longrightarrow H_2 + P- \qquad --(5)$$

In the above, P represents the protector and PH and P- represent the corresponding radicals. The following equation can be derived by steady state treatment of the above mechanism (analogous to cyclohexane)

$$\left\{1 + w \frac{(P)}{(C_2H_5OH)}\right\} \frac{I}{d(H_2)/dt} = 1 + v \left\{\frac{(P)}{(C_2H_5OH)}\right\} = \rho$$

where $w = k_5/k_3$, $v = (k_4 + k_5)/k_3$ and ρ represents the left hand side of the equation.

The numerical values of $I / \frac{d(H_2)}{dt}$ can be determined from the experimental data.

By giving arbitrary values to w, sets of values of ρ were calculated. These sets of values were plotted against the ratio $(P)/(C_2H_5OH)$ to see if a straight line could be obtained for each of benzene and cyclohexene.

The values of ρ which best fits the experimental data and the corresponding values of $I / \frac{d(H_2)}{dt}$ are presented in Tables XLII and XLIII. The lines obtained are shown in Figure 19. The values of the various ratios of rate constants are summarised in Table XLIV.

It is apparent that the values obtained for the rate constant ratios are rather similar in the cyclohexane and ethanol systems (see Tables XXVII and XLIV). While this similarity between the reactivities of ethanol and cyclohexane is not surprising (the rates of reaction of methyl radicals with cyclohexane and ethanol are approximately equal at 182°C and their activation energies are similar (138,pp 200 - 201)), the same comments that were made earlier in the case of cyclohexane can be repeated here. The values of the rate constant ratios obtained with cyclohexene might not be unreasonable if the hydrogen atoms are epithermal. However, the value of k_5/k_3 obtained from benzene is surprisingly high, even for epithermal hydrogen atoms. It implies that abstraction

TABLE XLII

Data for the Curve Fitting the (-196°C) Fraction Yield in Ethanol-Benzene Systems

Scavenging mechanism w = 0.9 b = benzene E = ethanol

1 ϵ_b	2 $G(H_2)_{obs}$ **	3 (b)/(E)	4 $I = 11.2\epsilon_E$	5 $G(H_2)^\circ_b \epsilon_b$	6 (2-5)*	7 (4/6)* = I / dH_2/dt	8 $1+w\frac{(b)}{(E)}$	9 $\rho = (7 \times 8)$*
0.0000	11.20	0.0000	11.20	0.000	11.20	1.00	1.000	1.00
0.0211	10.90	0.1333	10.96	0.032	10.87	1.01	1.012	1.02
0.0317	9.90	0.0202	10.84	0.048	9.85	1.10	1.018	1.12
0.0842	8.37	0.0569	10.26	0.126	8.24	1.25	1.051	1.31
0.1961	6.07	0.1505	8.90	0.294	5.78	1.54	1.135	1.75
0.5139	2.80	0.6544	5.44	0.771	2.00	2.72	1.590	4.32
1.0000	1.51	-	-	1.510	-	-	-	-

* These numbers refer to the number of the column, e.g., (2-5) means column (2) - column (5)

** G(-196°C) is taken as a measure of $G(H_2)$. The numbers in column 2 are really the yields of gases volatile at -196°C

TABLE XLIII

Data for the Curve Fitting the (-196°C) Fraction Yield in Ethanol-Cyclohexene Systems

Scavenging mechanism w = 20 o = cyclohexene E = ethanol

1 ϵ_o	2 $G(H_2)^{**}_{obs}$	3 (o)/(E)	4 $I = 11.2\epsilon_E$	5 $G(H_2)^{\circ}_{o}\epsilon_o$	6 (2-5)*	(4/6)* = 7 I / dH_2/dt	8 $1+w\frac{(o)}{(E)}$	9 $\rho = (7 \times 8)^*$
0.0000	11.20	0.0000	11.20	0.000	11.20	1.00	1.000	1.00
0.0101	8.44	0.0058	11.09	0.034	8.41	1.32	1.116	1.47
0.0202	7.11	0.0117	10.97	0.069	7.04	1.56	1.230	1.92
0.0406	5.97	0.0237	10.75	0.138	5.83	1.84	1.470	2.70
0.0810	4.80	0.0499	10.29	0.275	4.52	2.28	1.990	4.54
0.1897	3.90	0.1320	9.08	0.645	3.26	2.79	3.640	10.16
0.5034	3.40	0.5737	5.56	1.712	1.70	3.27	12.470	40.80
1.0000	3.38	-	-	3.380	-	-	-	-

* These numbers refer to the number of the column, e.g., (2-5) means column (2) - column (5)

** $G(-196^{\circ}C)$ is taken as a measure of $G(H_2)$. The numbers in column 2 are really the yields of gases volatile at -196°C

Figure 19

Figure 19

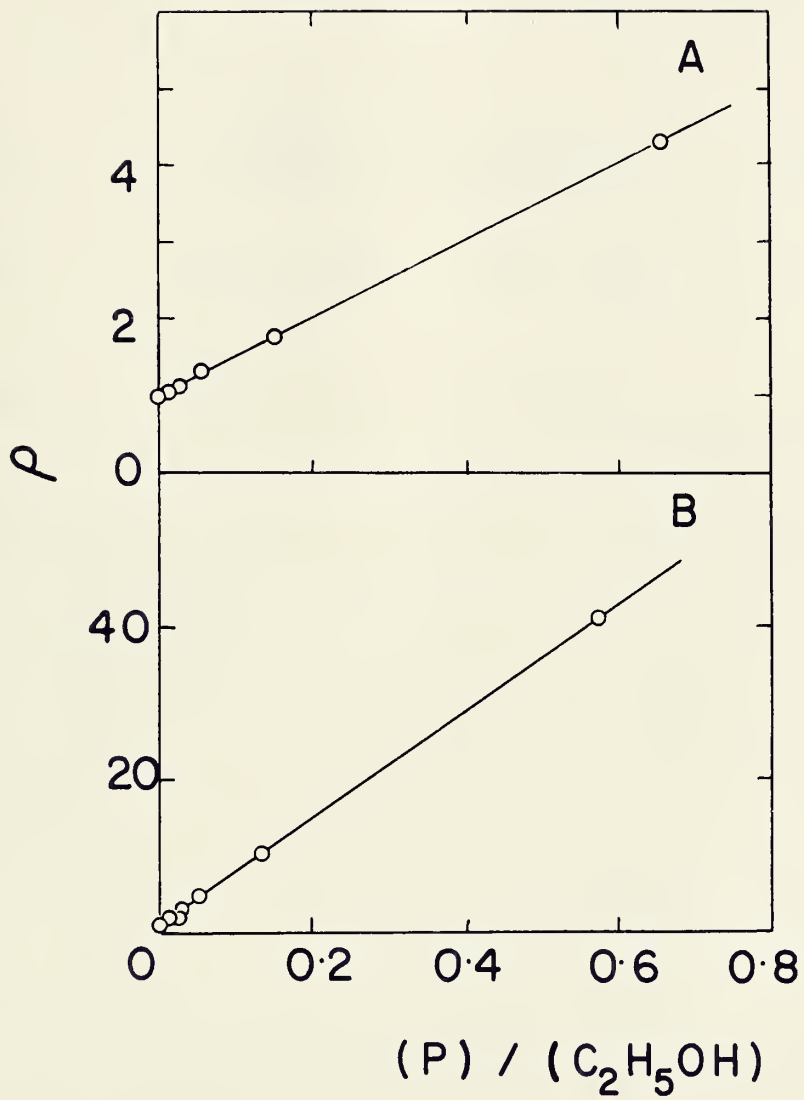
Kinetic Plots of Scavenging Mechanism

(Ethanol inhibition experiments)

$$\rho = \left\{1 + w \frac{(P)}{(E)}\right\} \frac{I}{d(H_2)/dt}$$

A: P = benzene

B: P = cyclohexene


A
B
4
2
0
40
20
0
0·2
0·4
0·6
0·8
ρ
(P) / (C2H5OH)

of hydrogen atoms from benzene is as easy as from ethanol. The much stronger C-H bond in benzene than in ethanol makes this seem unlikely.

Now consider the second mechanism.

(2) Energy (ionisation or excitation) transfer mechanism

$$C_2H_5OH \longrightarrow C_2H_5OH^* \qquad --(1)$$

$$C_2H_5OH^* \longrightarrow H_2 + \text{products} \qquad --(6)$$

$$C_2H_5OH^* + P \longrightarrow C_2H_5OH + P^* \qquad --(7)$$

$$P^* \longrightarrow x\ H_2 + \text{products},\ 0 \leq x \leq 1 \qquad --(8)$$

The x signifies that perhaps not every P^* results in the formation of an H_2. Reactions (6) and (8) represent over-all processes and might comprise several steps each. Steady state treatment of this mechanism yields (analogous to cyclohexane energy transfer mechanism)

$$\left[1 + y\ (P)\right]\left[I\ /\ d(H_2)/dt\right] = 1 + z\ (P) = \rho'$$

where $y = x\ k_7/k_6$, $z = k_7/k_6$ and ρ' represents the left hand side of the equation.

Assuming arbitrary values for y, sets of values of ρ' were calculated and plotted against the protector

concentration, (P), in an attempt to obtain a straight line with an intercept of unity. Figure 20 shows the lines that were obtained (see also Tables XLV and XLVI). The value of y that gave the desired line in each system, along with the slope of the line, z, and the corresponding value of x is presented in Table XLVII.

(E) Summary of the Values of Ratios of Rate Constants in the Various Systems

A summary of the values of rate constant ratios is presented in Tables XLVIII and XLIX.

An examination of Table XLVIII reveals that the various ratios appear to have similar values in the three systems. The value of k_4/k_5 for methyl cyclohexane systems could not be calculated because of lack of precision in the values of k_5/k_3. The various ratios in Table XLIX also appear to have similar values except for the ethanol-benzene system.

It does not seem useful to speculate here upon the possible reasons for these similarities and differences. No definite conclusion can yet be drawn concerning the identity of the activated substrate species. Further work, especially using compounds with widely differing ionisation potentials and hydrogen atom activities, is required.

It may be remarked, however, that one possible

reason for the lack of resolution between these two mechanisms might be that they both occur to comparable extents. Two mechanisms do occur to comparable extents in the liquid cyclohexane systems (58).

TABLE XLV

Data for the Curve Fitting the (-196°C) Fraction Yield in Ethanol-Benzene Systems

Energy transfer mechanism y = 6 b = benzene E = ethanol

1 ϵ_b	2 $G(H_2)_{obs}$**	3 b(moles/L) gas phase	4 $I = 11.2\epsilon_E$	5 $G(H_2)^\circ_b\epsilon_b$	6 (2-5)*	7 (4/6)* $= I/dH_2/dt$	8 $1 + y$ (b)	9 $\rho' = (7 \times 8)$*
0.0000	11.20	0.000	11.20	0.000	11.20	1.00	1.000	1.00
0.0211	10.90	0.372	10.96	0.032	10.87	1.01	1.002	1.01
0.0317	9.90	0.557	10.84	0.048	9.85	1.10	1.003	1.10
0.0842	8.37	1.486	10.26	0.126	8.24	1.25	1.009	1.26
0.1961	6.07	3.474	8.90	0.294	5.78	1.54	1.021	1.57
0.5139	2.80	9.288	5.44	0.771	2.00	2.72	1.056	2.87
1.0000	1.51	-	-	1.510	-	-	-	-

* These numbers refer to the number of the column, e.g., (2-5) means column (2) - column (5)

** G(-196°C) is taken as a measure of $G(H_2)$. The numbers in column 2 are really the yields of gases volatile at -196°C

TABLE XLVI

Data for the Curve Fitting the (-196°C) Fraction Yield in Ethanol-Cyclohexene Systems

Energy transfer mechanism y = 720 o = cyclohexene E = ethanol

1 ϵ_o	2 $G(H_2)^{**}_{obs}$	3 o(moles/L) gas phase	4 $I = 11.2\epsilon_E$	5 $G(H_2)^{\circ}_{o}\epsilon_o$	6 (2-5)*	7 (4/6)* = $I/dH_2/dt$	8 $1 + y\ (o)$	9 $\rho' = (7 \times 8)^*$
0.0000	11.20	0.0000	11.20	0.000	11.20	1.00	1.000	1.00
0.0101	8.44	0.1629	11.09	0.034	8.41	1.32	1.117	1.47
0.0202	7.11	0.3257	10.97	0.069	7.04	1.56	1.235	1.93
0.0406	5.97	0.6514	10.75	0.138	5.83	1.84	1.469	2.70
0.0810	4.80	1.3028	10.29	0.275	4.52	2.28	1.938	4.42
0.1897	3.90	3.0453	9.08	0.645	3.26	2.79	3.193	8.91
0.5034	3.40	8.1423	5.56	1.712	1.70	3.27	6.862	22.44
1.0000	3.38	-	-	3.380	-	-	-	-

* These numbers refer to the number of the column, e.g., (2-5) means column (2) - column (5)

** $G(-196^{\circ}C)$ is taken as a measure of $G(H_2)$. The numbers in column 2 are really the yields of gases volatile at -196°C

Figure 20

Figure 20

Kinetic Plots of Energy Transfer Mechanism

(Ethanol inhibition experiments)

$$\rho' = \left[1 \quad y\,(P)\right]\left[\; I \;/\; d(H_2)/dt\right]$$

A: P = benzene

B: P = cyclohexene

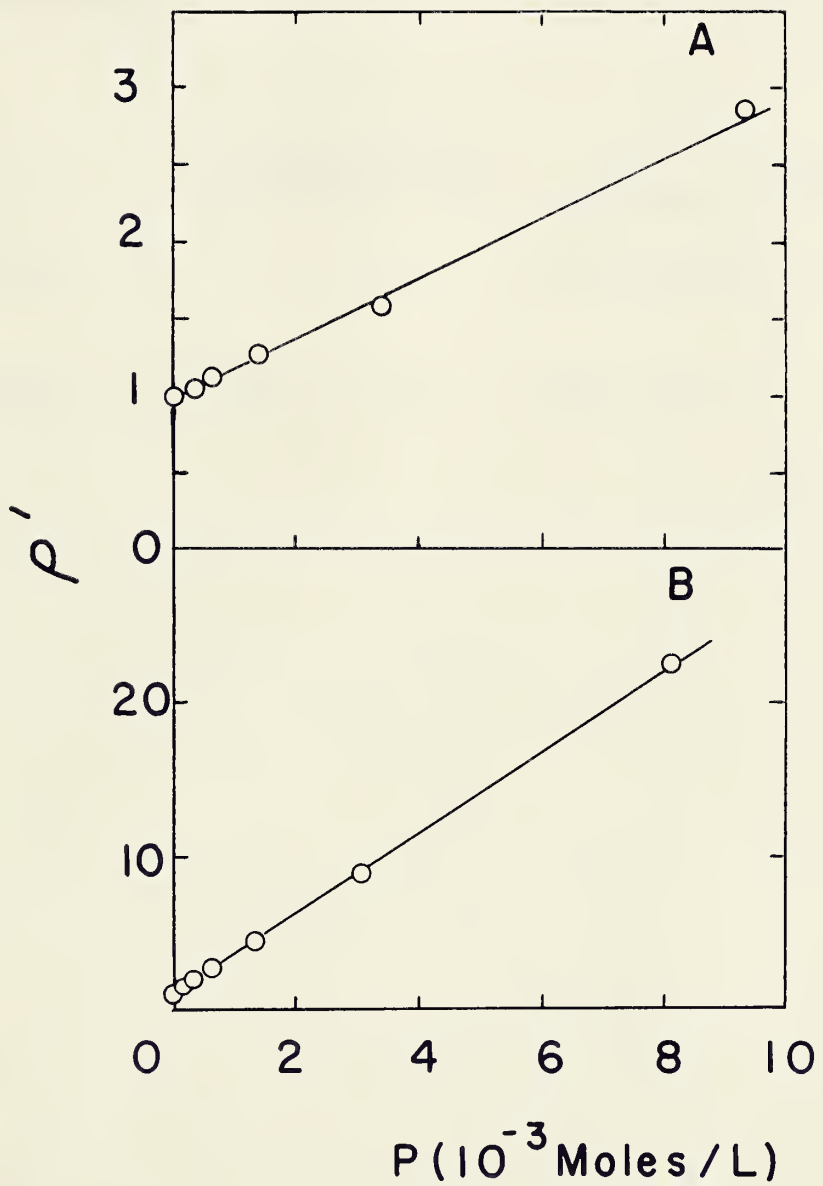

A
B
3
2
1
0
20
10
0
2
4
6
8
10
ρ'
P (10⁻³ Moles / L)

TABLE XLVII

Values of Kinetic Parameters Obtained from Energy Transfer Mechanism

P	y(litres/mole)	x	z(k_7/k_6, litres/mole)
C_6H_6	6 ± 6	0.03 ± 0.03	190 ± 20
C_6H_{10}	720 ± 180	0.28 ± 0.01	2600 ± 600

TABLE XLVIII

Summary of Values of Kinetic Parameters Obtained from Scavenging mechanism in the Various Systems.

P	Solvent	k_5/k_3	k_4/k_3	k_4/k_5
C_6H_6	C_6H_{12}	2.5 ± 0.2	5.9 ± 0.5	2.4
	C_7H_{14}	3 ± 3	2.6 ± 0.2	-
	C_2H_5OH	0.9 ± 0.3	4.2 ± 0.5	4.7
C_6H_{10}	C_6H_{12}	25 ± 10	31 ± 19	1.2
	C_7H_{14}	> 5	> 9	-
	C_2H_5OH	20 ± 5	50 ± 10	2.5

TABLE XLIX

Summary of Values of Kinetic Parameters Obtained from Energy Transfer Mechanism in the Various Systems

P	Solvent	y(litres/mole)	x	z(k_7k_6, litres/mole)
C_6H_6	C_6H_{12}	150 ± 18	0.25 ± 0.01	610 ± 25
	C_7H_{14}	600 ± 540	0.5 ± 0.2	1000 ± 800
	C_2H_5OH	6 ± 6	0.03 ± 0.03	190 ± 20
C_6H_{10}	C_6H_{12}	1200 ± 420	0.44 ± 0.01	2700 ± 800
	C_7H_{14}	≃ 600*	≃ 0.4 ± 0.1	≃ 1500*
	C_2H_5OH	720 ± 180	0.28 ± 0.01	2600 ± 600

* within a factor of 2

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